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Fuel retention properties in first wall materials: the influence of displacement damage, microstructure, and helium

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WP PFC, WP PWIE, WP MAT-IREMEV

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Fuel retention properties in tungsten: the influence of displacement damage, microstructure, and helium

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Outline

- Introduction / Motivation

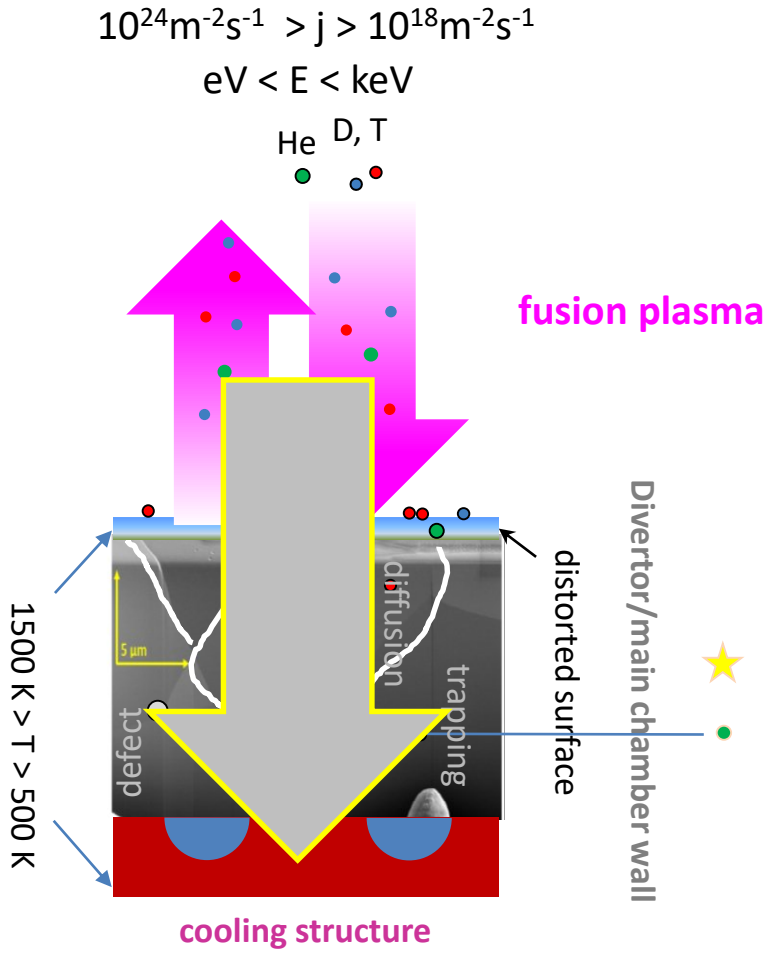
- Deuterium retention in W-irradiated W and the effect of:
  - annealing
  - D presence
  - defects on D location in the tungsten
  - He in the bulk and at the surface
  - Influence of microstructure – grain boundaries

- Conclusion

Motivation

Simplified plasma-wall interaction

Tungsten – plasma facing material – first wall and divertor



- Last ten years the focus was on displacement damage

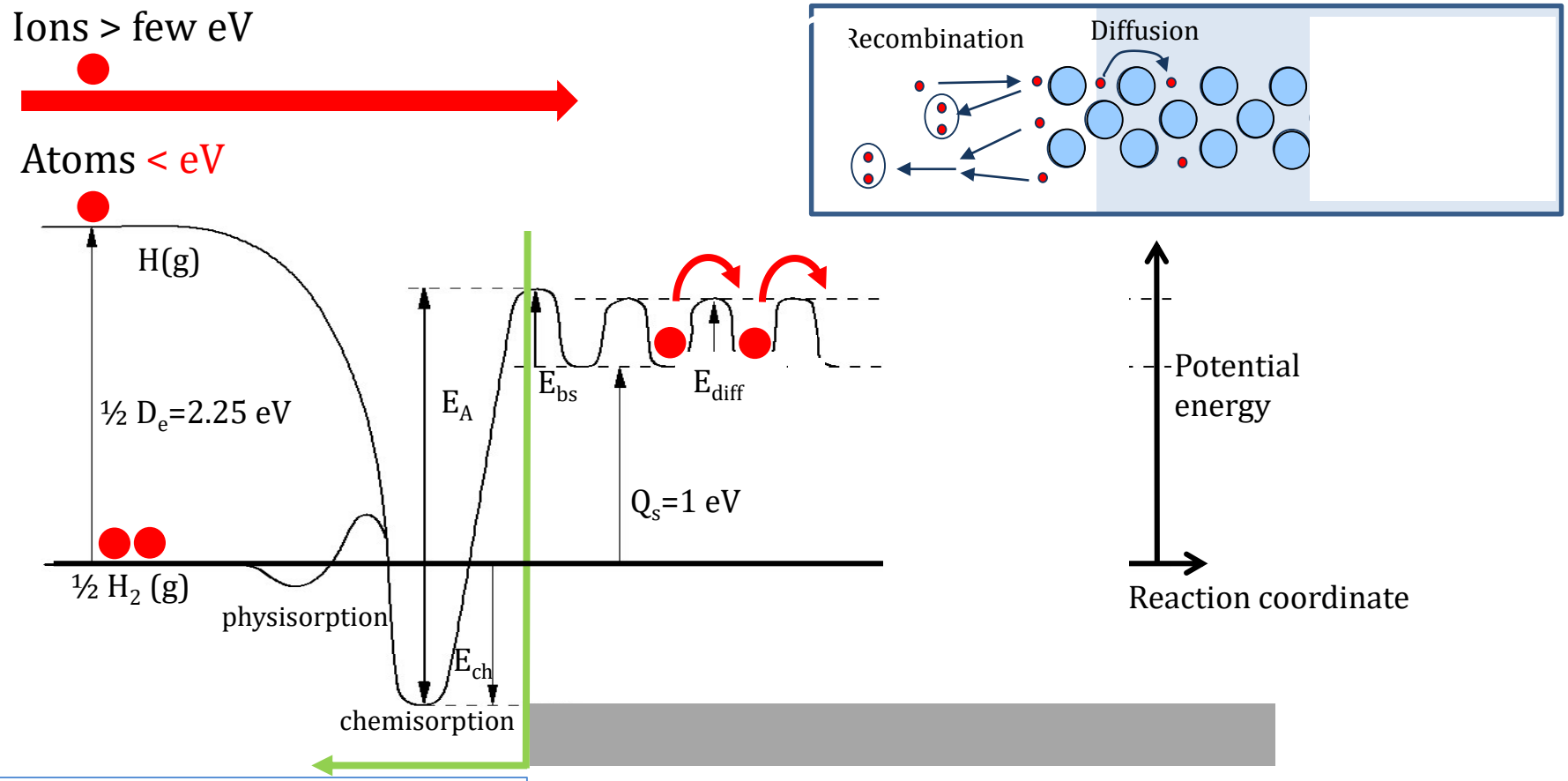
★ neutron damage – 5 dpa/fpy [1]

● He production

Transmutations,…

[1] Federici et al., Nucl. Fusion 57 092002, 2017

Hydrogen interaction picture (kinetics and dynamics): energy potential



W bulk parameters

E_{diff} =0.39 eV (0.28 eV)

Q_s= 1.04 eV

E_A ≈ 2 eV

[Frauenfelder 1969 *J. Vac. Sci. Technol.; Holzner et al. Phys. Scr. T171, 014034 (2020).*]

- Hydrogen transport is driven by fast diffusion of solute atoms

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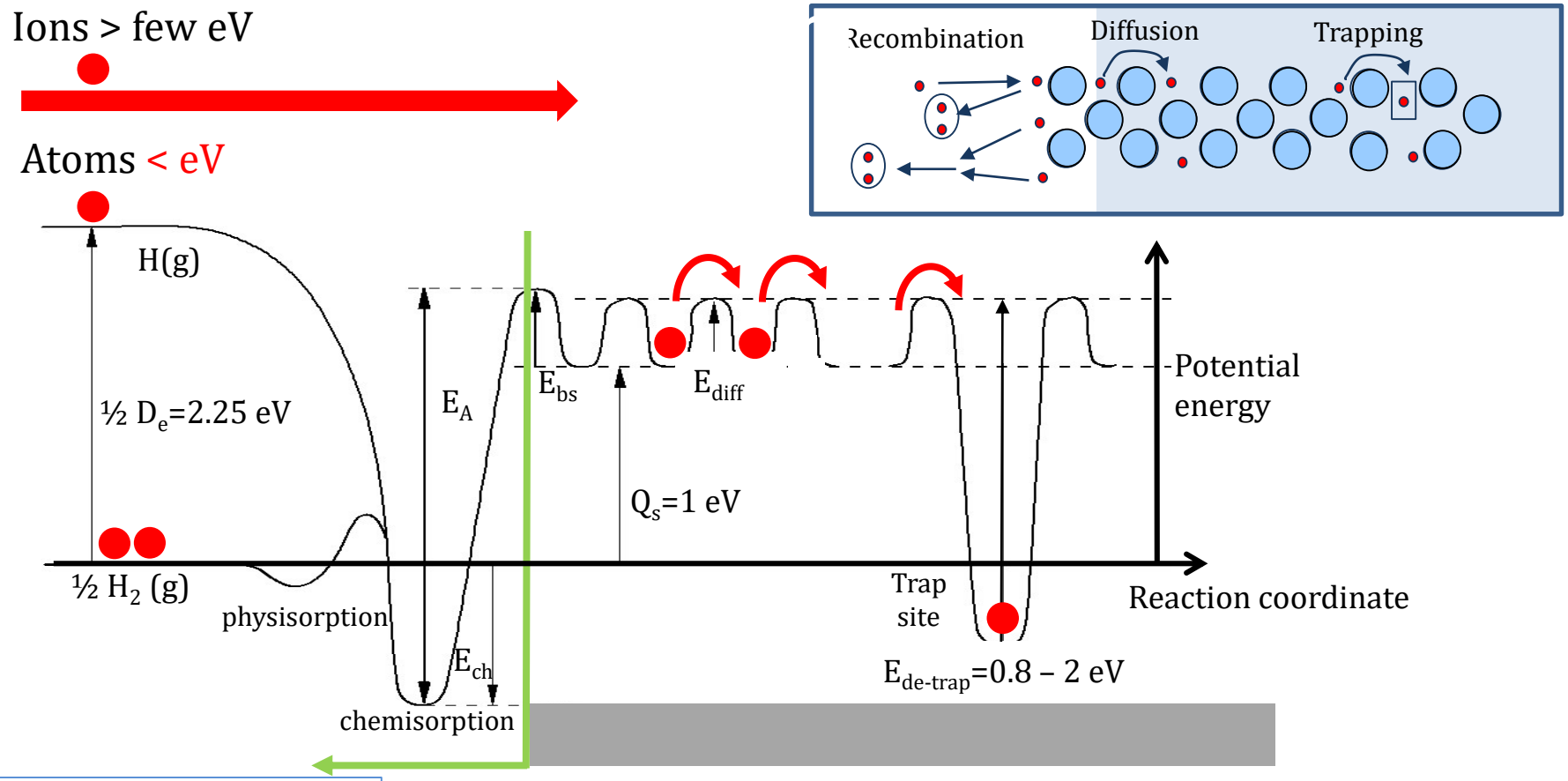

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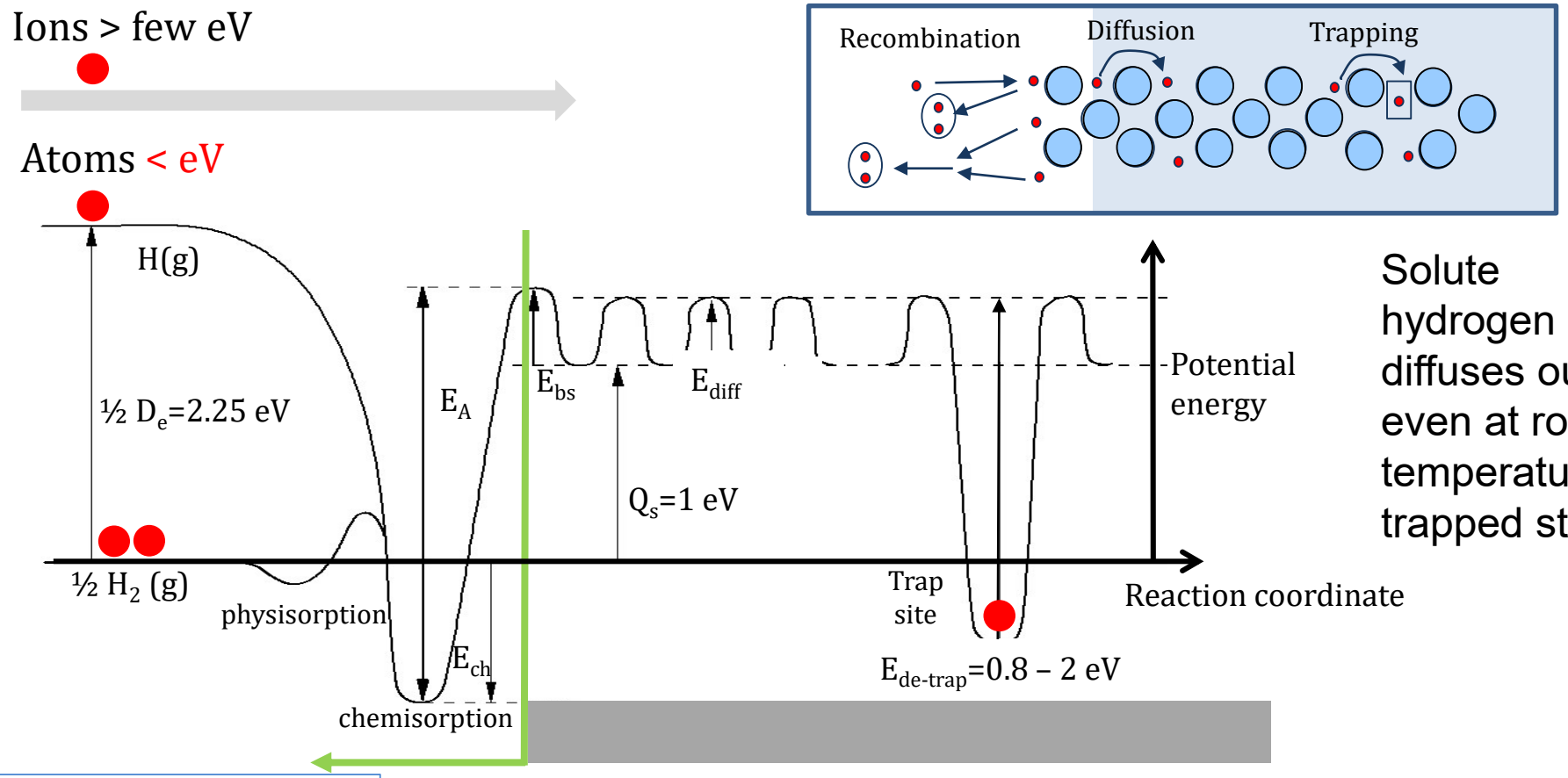
- Hydrogen transport is driven by fast diffusion of solute atoms
- Hydrogen trapping slows down transport

Hydrogen interaction picture (kinetics and dynamics): energy potential diagram

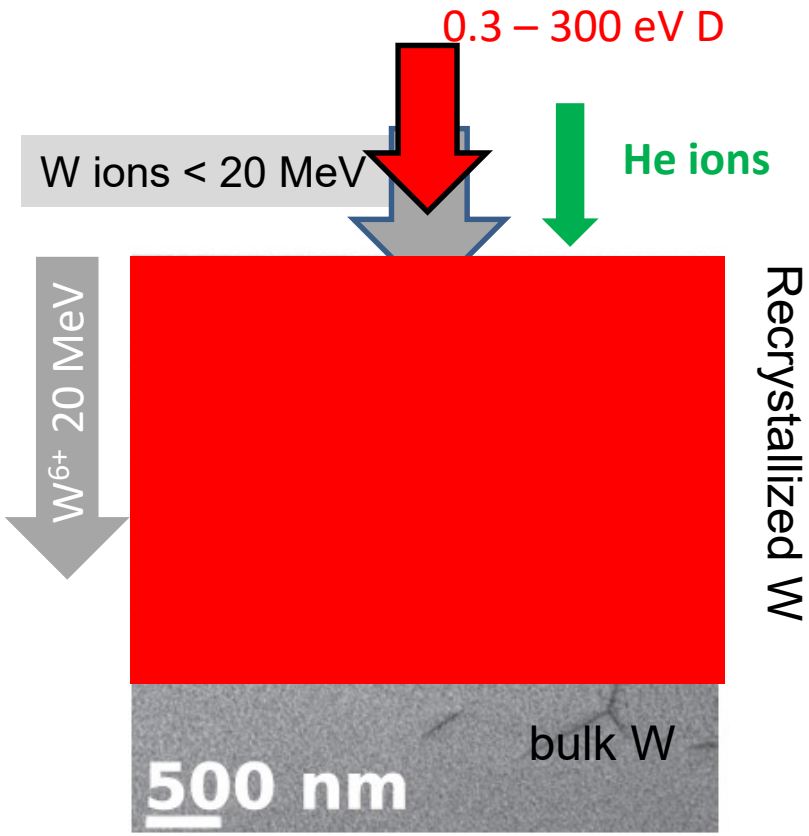


Solute hydrogen diffuses out even at room temperature, trapped stays

W bulk parameters
E$_{diff}$ =0.39 eV (0.28 eV)
Q$_s$= 1.04 eV
E$_A$ ≈ 2 eV
[Frauenfelder 1969 *J. Vac. Sci. Technol.*]

- Hydrogen transport is driven by fast diffusion of solute atoms
- Hydrogen trapping slows down transport
- Hydrogen inventory-retention is determined by trapped hydrogen

Separating individual aspects of the interaction



Damaged layer characterization by Scanning Transmission Electron Microscopy (STEM) [Založnik et al. Phys Scr. T167 (2016) 014031]

W ion irradiation by MeV W ions
- Creation of displacement damage
- Dense cascades

He irradiations (bulk and surface) later

- Exposure to D atoms/ions – to only populate the existing traps without producing new ones
- Open volume defects are traps for hydrogen isotopes [S. M. Myers et al., JNM 165 (1989) 9–64]

Methodology to quantify D retention, defect evolution and defect concentration:

- **measure D concentration by nuclear reaction analysis (NRA) via $D(^3He,p)^4He$**
- **desorption kinetics by thermal desorption spectroscopy (TDS)**
- **Use macroscopic rate equation modelling**

How to obtain defect densities and de-trapping energies

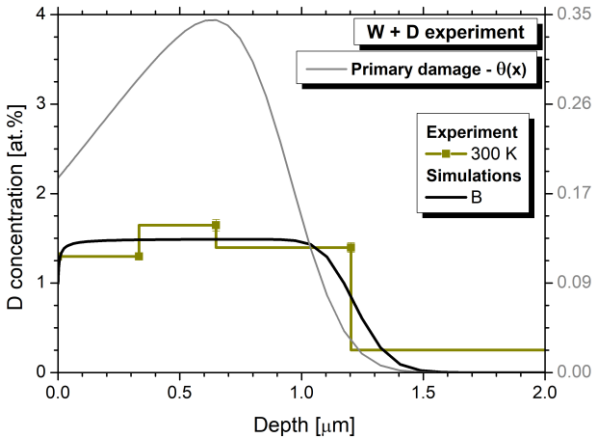
Determination of defect density and de-trapping energies: Fitting D depth profile and TDS spectrum by rate equation modelling codes (MHIMS, TESSIM)

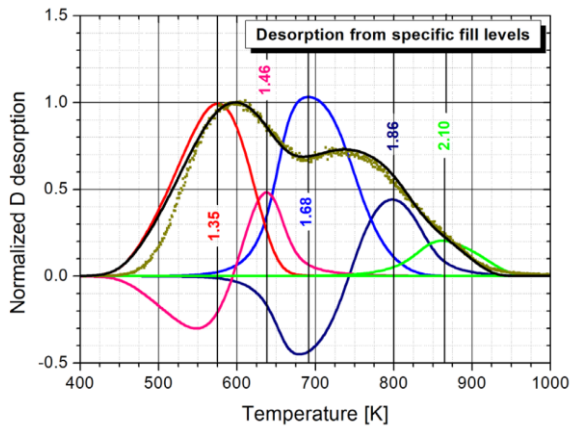
300 eV D exposure at 450 K

- ✓ Double peak
- ✓ Five de-trapping energies 1.35 eV - 2.09 eV

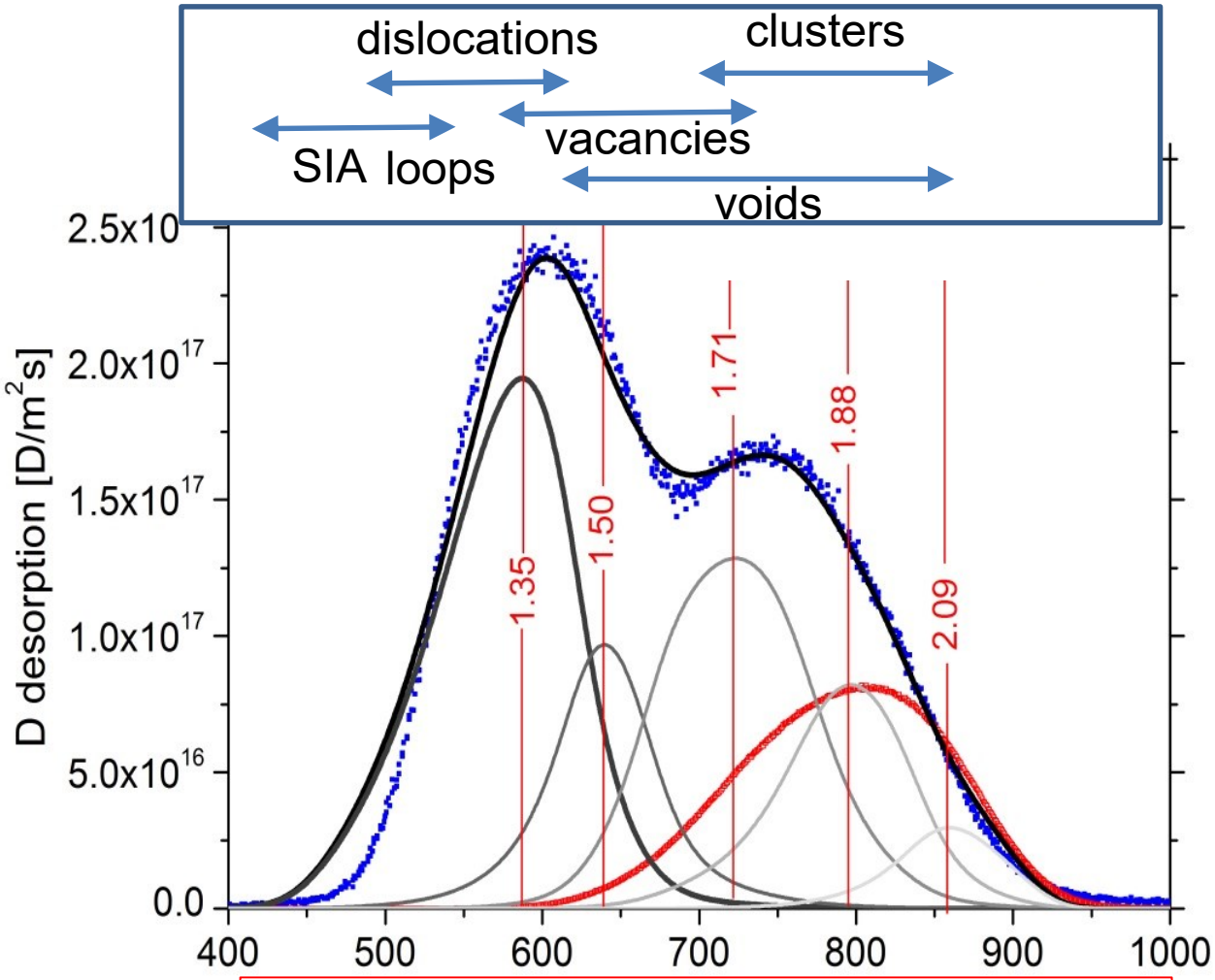
0.3 eV D exposure at 600 K

- ✓ Single peak
- ✓ 3x lower D amount
- ➢ **Active thermal detrapping!**
- ✓ Three de-trapping energies





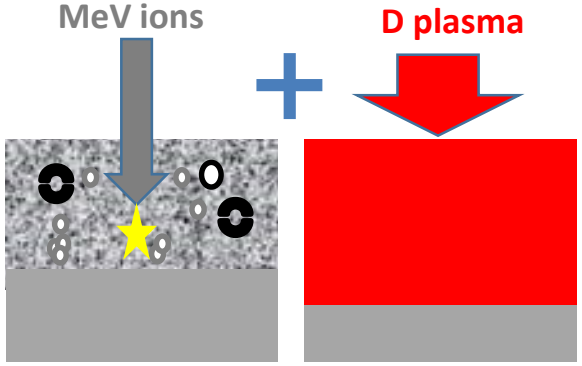
*M. Pečovnik et al. Nucl. Fusion **60,** 036024 (2020)*



Defect densities and de-trapping energies relevant for ITER / DEMO exposure scenarios?

Creation of displacement damage: dpa dependence at 290 K

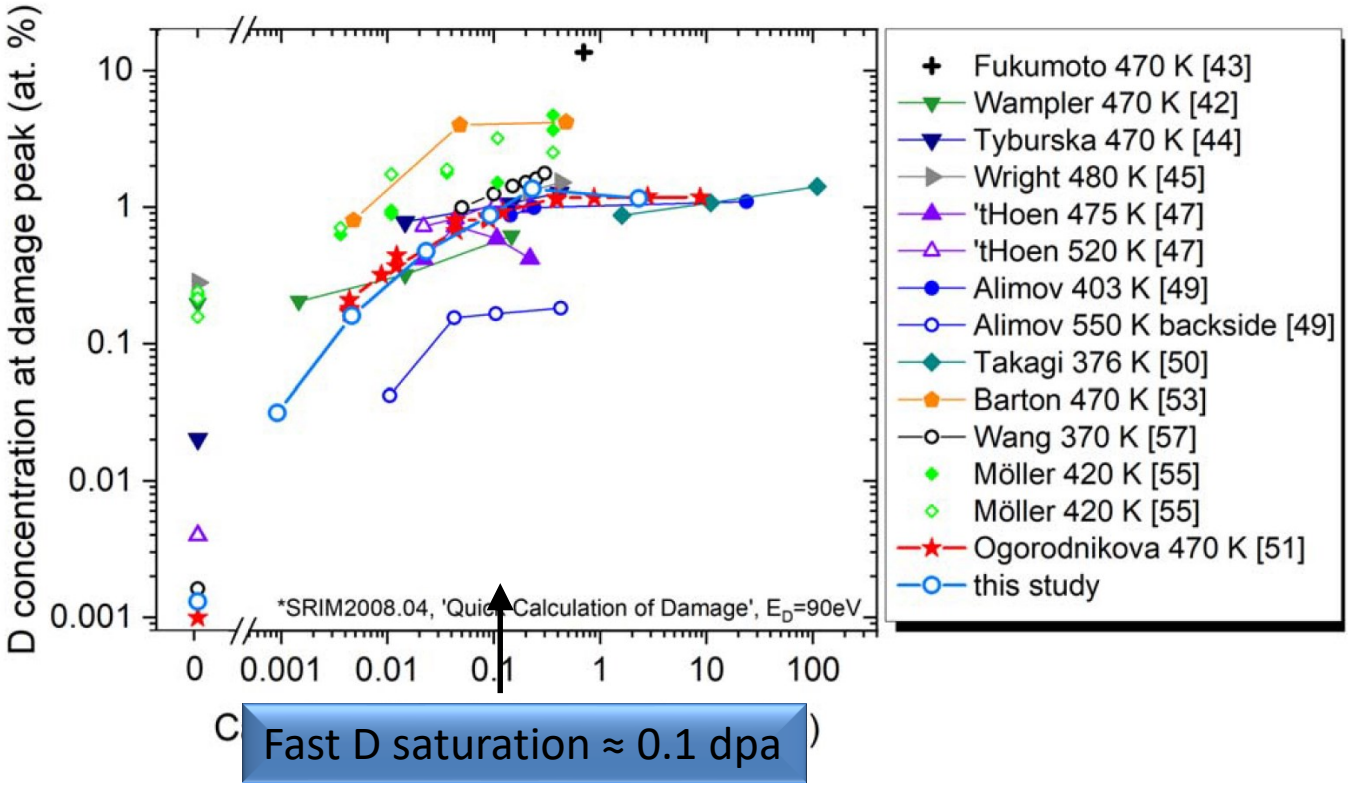
- Deuterium concentration as a function of damage dose (irradiation @ 290 K).



No displacement damage – D concentration 10^{-3} at. %
Small dpa < 0.03 – isolated defects, linear dependence on damage dose

High dpa > 0.1 – cascade overlap -> **saturation of D concentration @ 1 at. %**

- **Saturation of defect density 1 at. %**

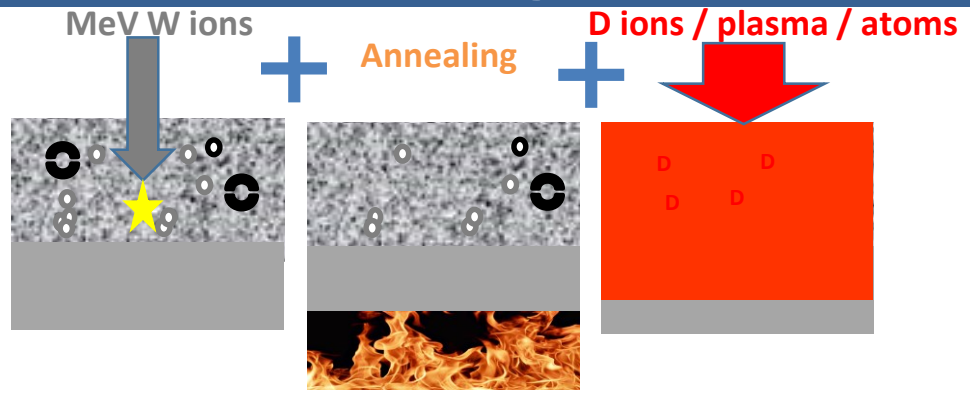


Dpa dependence at elevated temperatures?
Talk by M. Zibrov

- All further studies in damage saturation > 0.1 dpa

[T. Schwarz-Selinger, Mater. Res. Express 10 (2023) 102002]

Defect evolution with temperature: post annealing



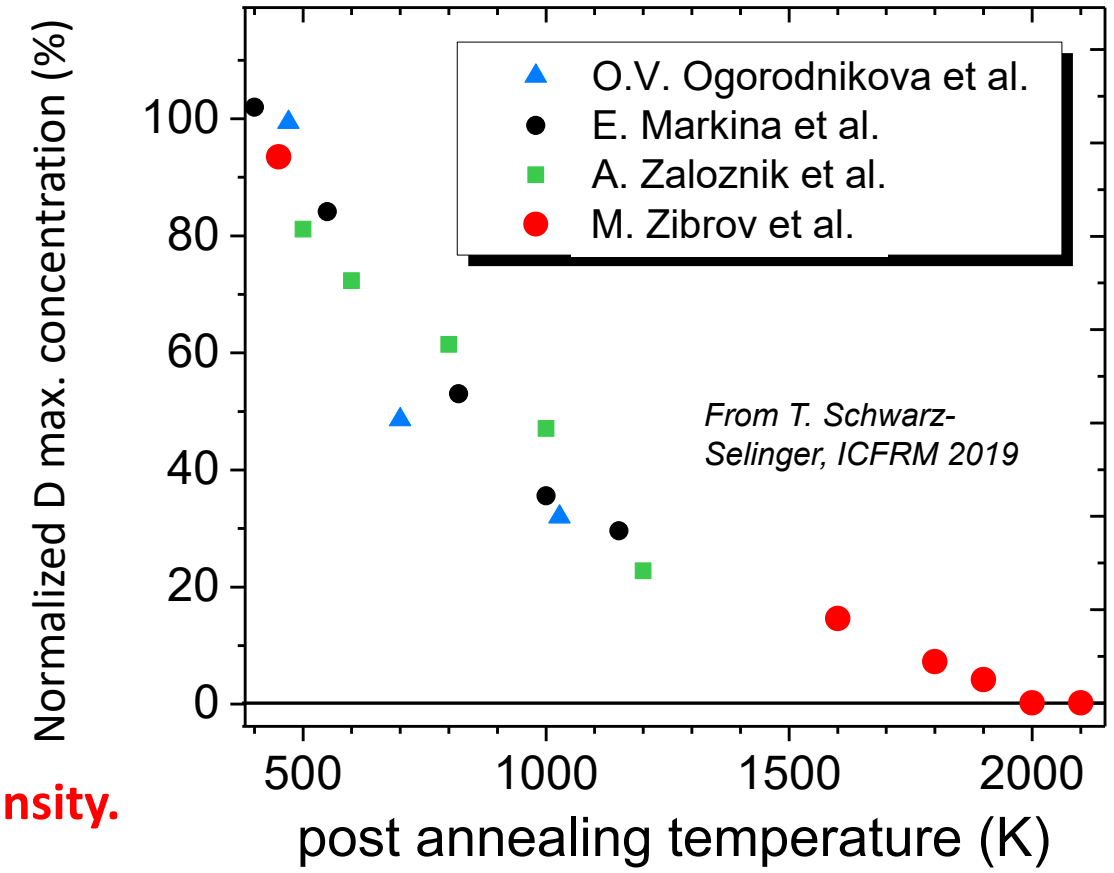
Damaging at room temperature and post-annealing:

- Vacancy migration above 500 K *[Keys and Moteff JNM 34 (1970) 260; A. Debelle et al., 376 (2008) 216-221]*
- Cluster migration, annihilation and coalescence at higher temperature
- Reduction of dislocation lines and loops [*F. Ferroni et al., Acta Mater. 90 (2015) 380–93*]

➢ **Reduction of D concentration - reduction in defect density.**

✓ **A complete recovery appears only above 2000 K**

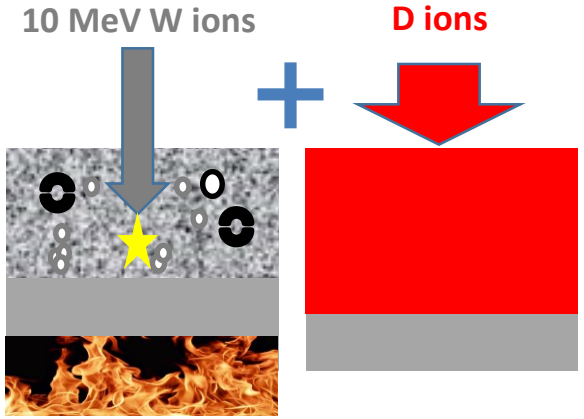
➢ Cluster migration, annihilation and coalescence – slight **suppression due to presence of D** *Pecovnik et al. Nucl. Fusion 60 (2020) 106028*



O.V. Ogorodnikova et al., J. Nucl. Mater. 451 (2014) 379–86.
E. Markina J. Nucl. Mater. 463 (2015) 329–32.
A. Založnik, Phys. Scripta T167 (2016) 014031.
M. Zibrov et al. NME 23 (2020) 100747

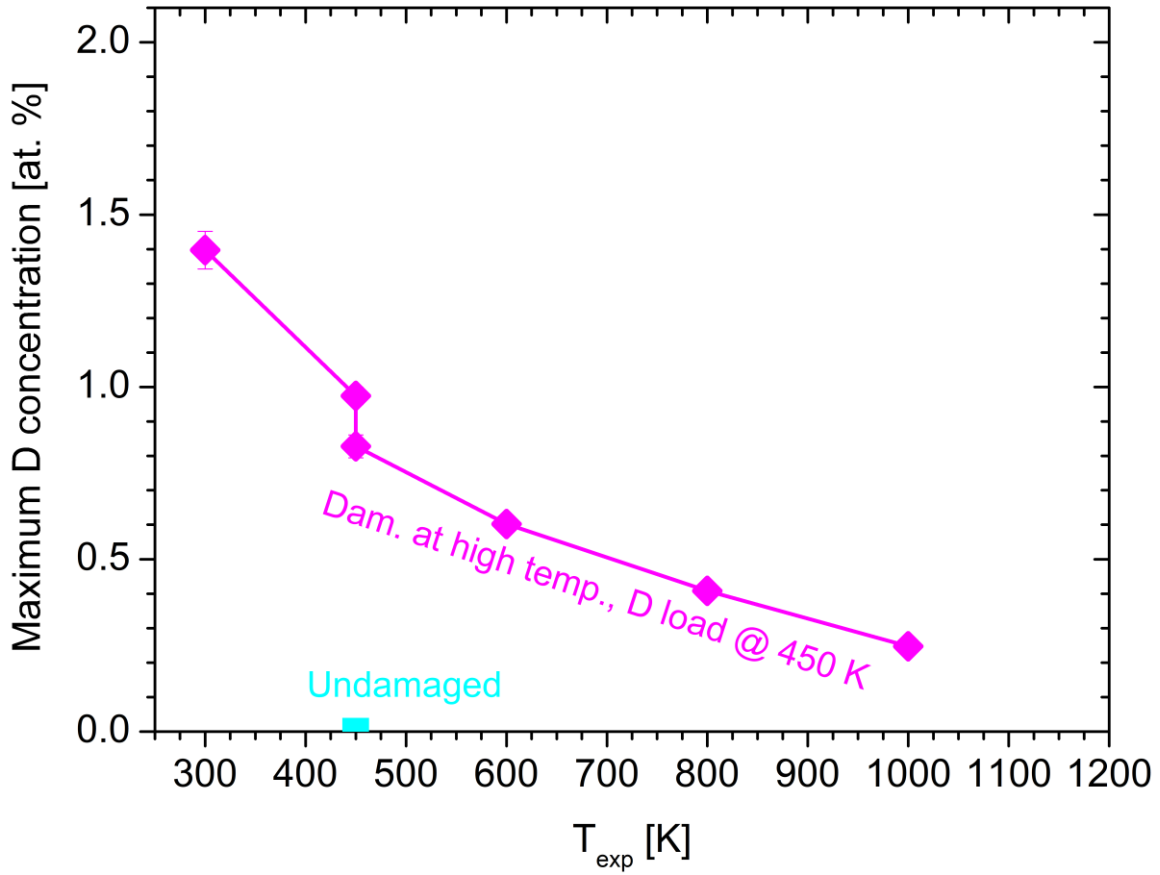
No model on defect annealing, do defects anneal during TDS?

W irradiation at elevated temperatures + sequential exposure to D

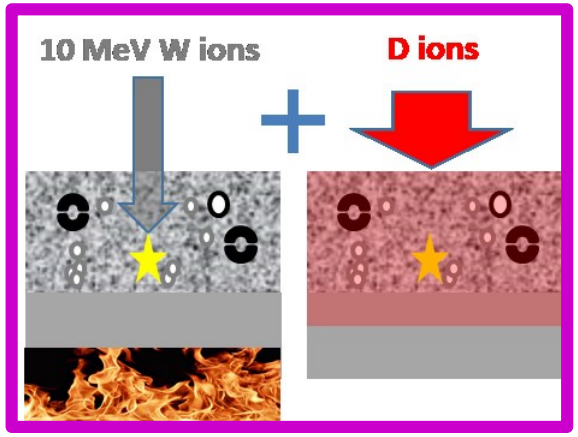


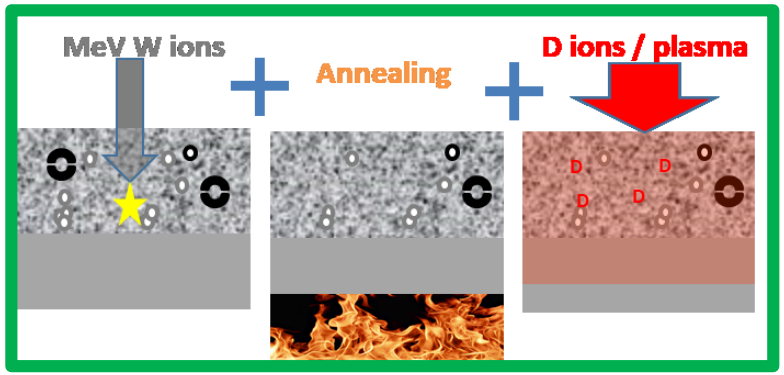
Damaging at high temp. (sequential) + 300 eV D exposure at 450 K

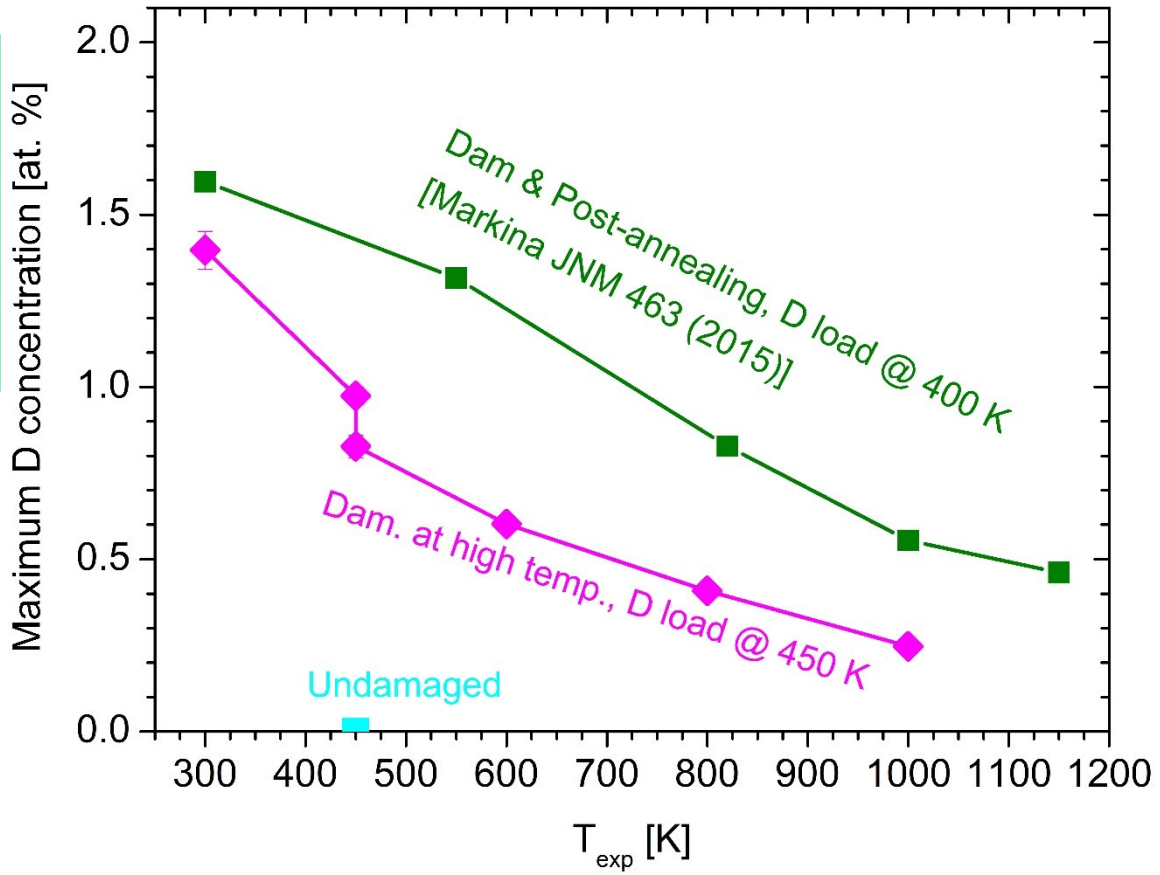
- D concentration decreases with irradiation temperature
- Less defects created at elevated temperatures



Defect evolution with temperature: irradiation at high temperatures versus post-annealing







Damaging at high temp. (sequential) + 300 eV D exposure at 450 K

- D concentration decreases with irradiation temperature
- Less defects created at elevated temperatures

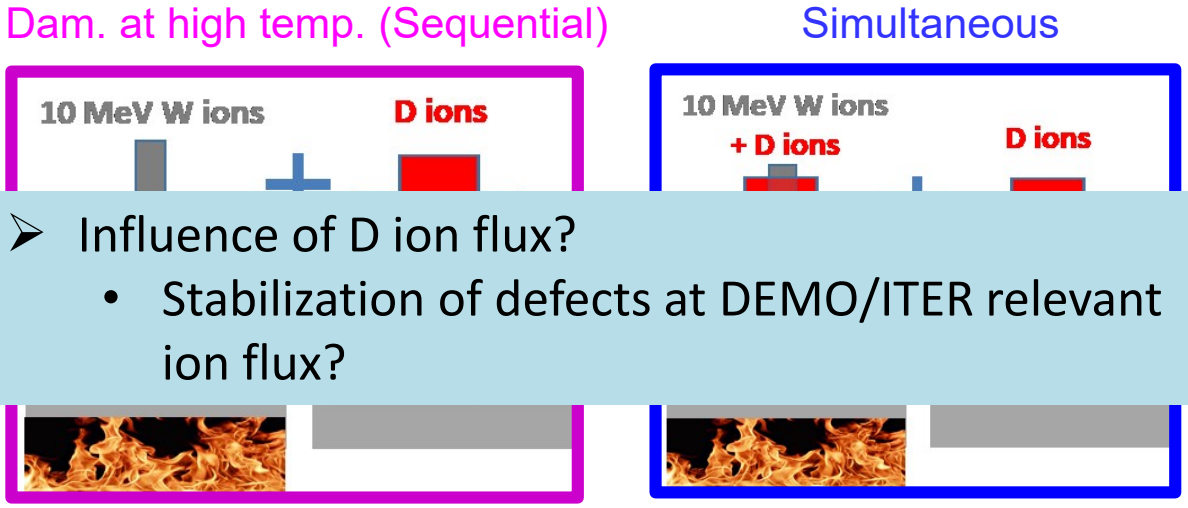
Damaging at 300 K and post-annealing + D @ 400 K

- Defects anneal with increase of temperature

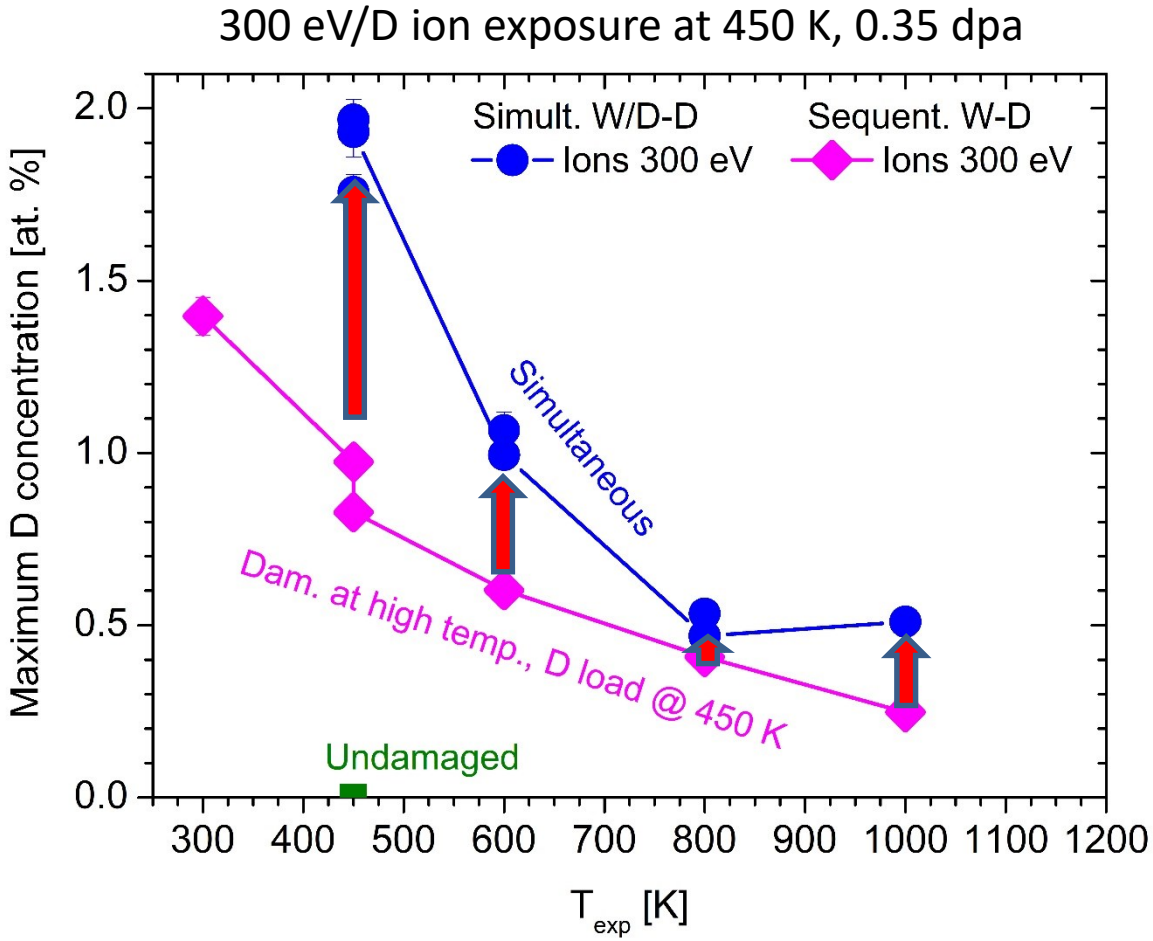
- Nearly 50 % less traps compared to post-annealing

⇒ Speculation: **Annealing of an evolving defect structure compared to annealing of large scale defects**

W irradiation at elevated temperatures with D + sequential exposure to D



- Influence of D ion flux?
  - Stabilization of defects at DEMO/ITER relevant ion flux?



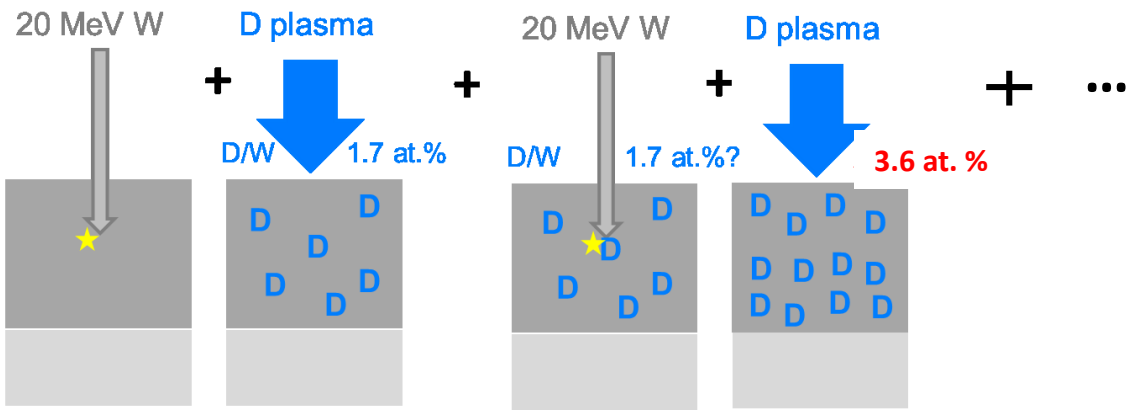
- Increase of D concentration (factor of two) – larger defect concentration due to presence of D
- Higher defect densities at low temperatures
- Reduced defect stabilization at high temperatures due to thermal detrapping of D during experiment for our D ion fluxes
- Increase of stabilization at T ≥1000 ? – ongoing study

- *Rate equation modelling to understand the observed phanomena – Model on defect stabilization due to trapping of D in defects [Pečovnik et al. Nucl. Fusion 60 (2020) 036024]*
- *First MD modelling that reproduces experimental observations [Lindbland, Mason and Granberg 2024 https://dx.doi.org/10.2139/ssrn.4808177]*

S. Markelj et al., Nuclear Fusion 59 (2019) 086050.

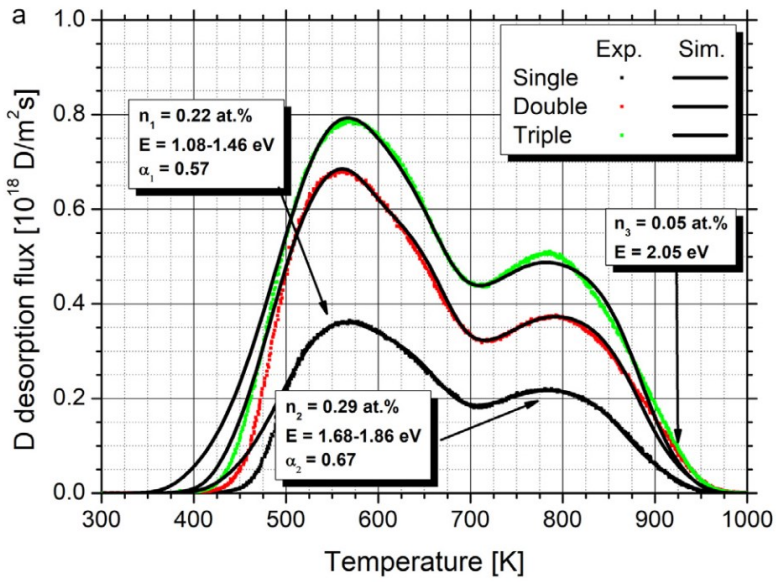
Influence of D presence on defect creation in W

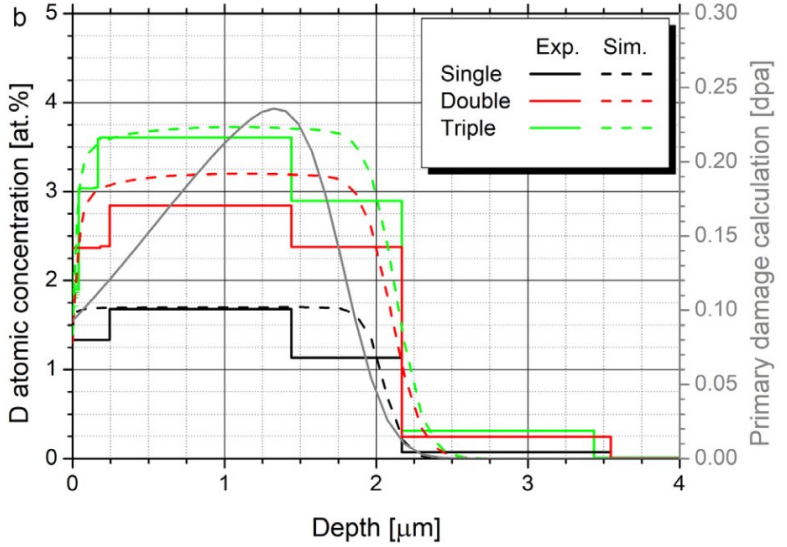
T. Schwarz-Selinger



Schwarz-Selinger et al. NME 17, 228–234 (2018).

- **Application of the *defect stabilization model* to different experiment**
- **D saturation concentration at 4.2 at.% is expected**
- *M. Pečovnik et al., J. Nucl. Mater.* ***550****, 152947 (2021)*





Summary on the defect densities and D trapping energies

All in all, 8 detrapping energies found – the same in all studies cases

- Defect densities change with temperature and exposure scenario (sequential / simultaneous)

Three defect types with several fill-levels:

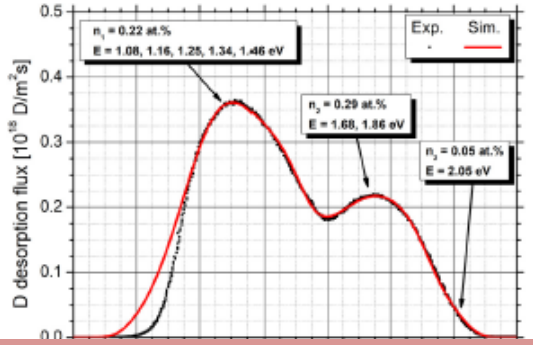
Defect type 1 – (1.08, 1.16, 1.25, 1.34, 1.46) eV;

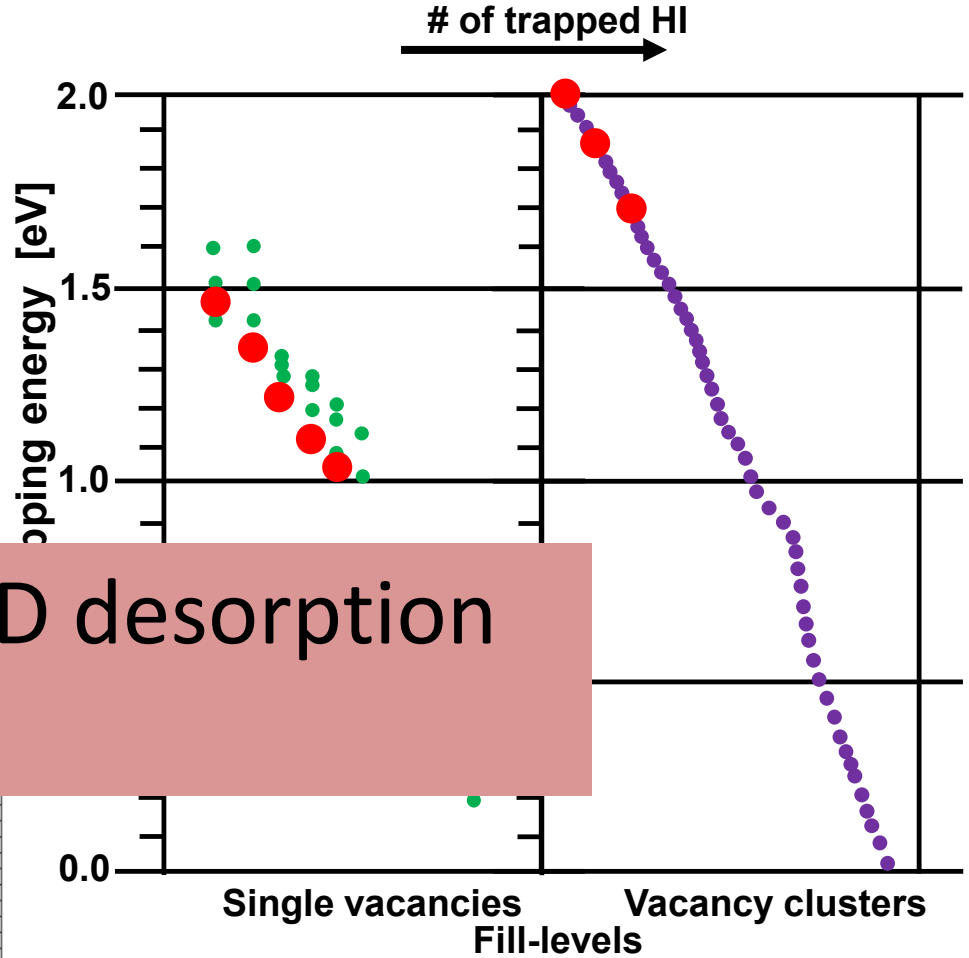
Defect type 2 – (1.68, 1.86) eV;

Defect type 3 – 2.05 eV.

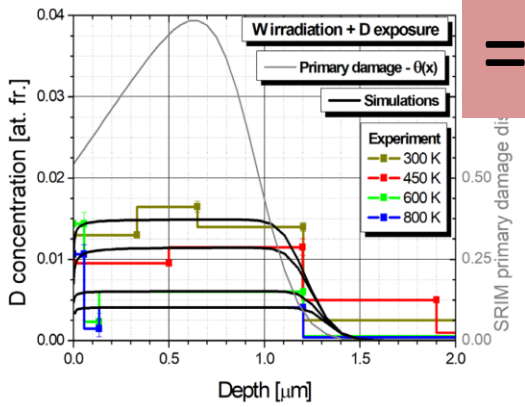
- Comparison to DFT calculations
  - Defect 1 -> single vacancies
  - Defect 2 -> small vacancy clusters
  - Defect 3 -> large vacancy clusters

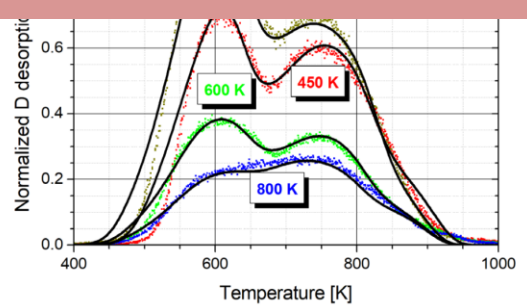
M. Pečovnik et al. Nucl. Fu
M. Pečovnik et al. , *Nucl. F*
M. Pečovnik et al., *J. Nucl.*

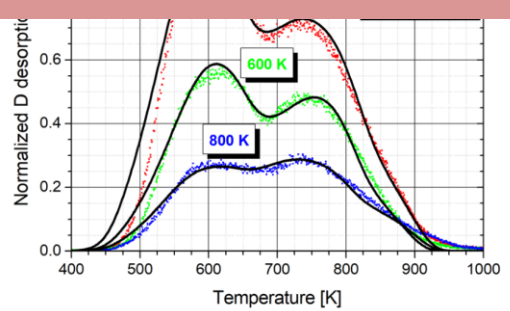




Fitting D depth profile and D desorption = "Engeneering approach"

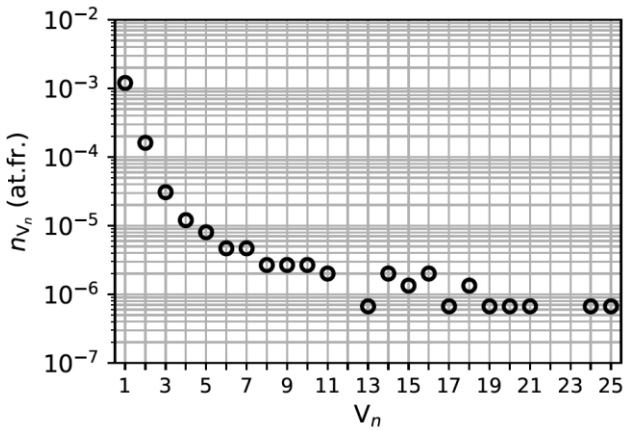




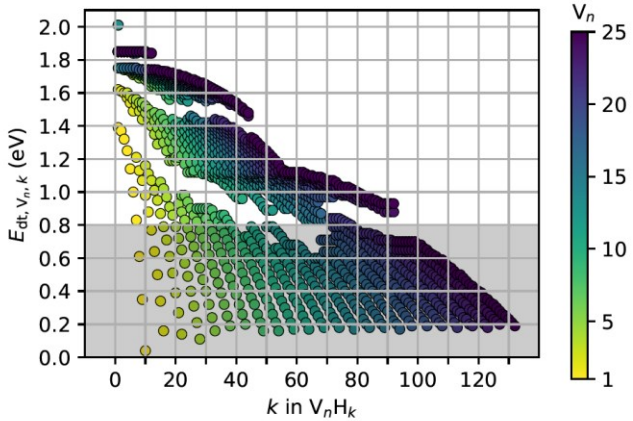


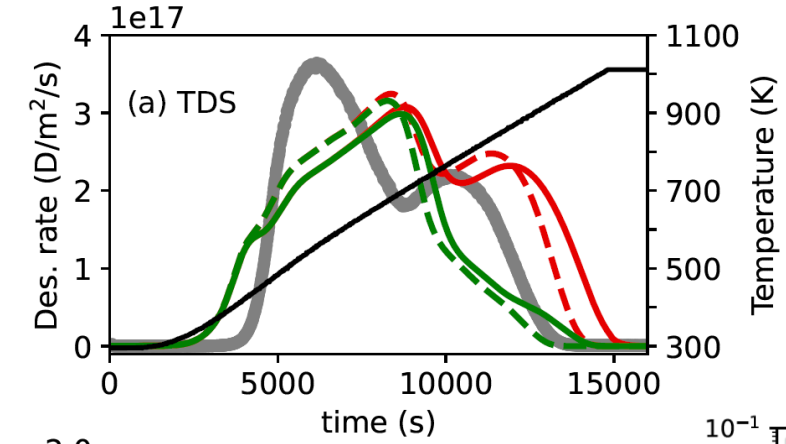
The “Physicist” approach (Hodille et al.)

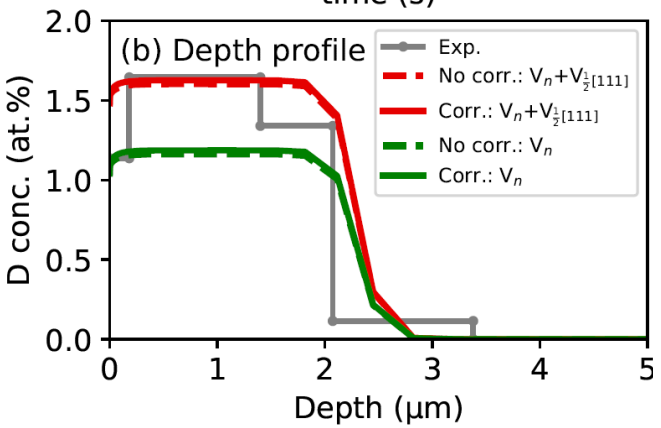
Take the concentration of the vacancy cluster Vn from the MD simulations (AT-ZN potential) of cumulative cascade up to 0.2 dpa *[F. Granberg et al. JNM 556 (2021) 153158]*

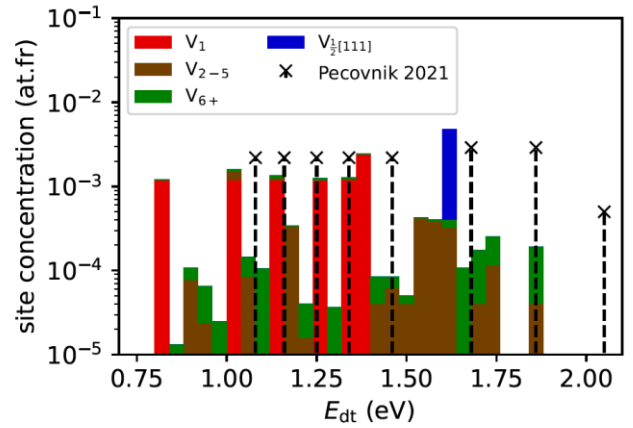


Detrapping energies for VnHk obtained with the model derived from DFT calculations *[J. Hou et al. Nature materials, 18 (2019) 833–839].*









- Agreement acceptable

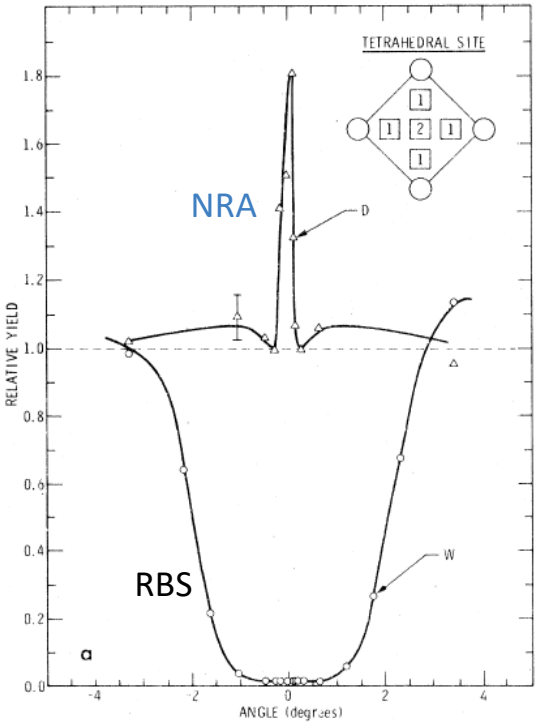
Hodille et al. PSI proceedings, submitted to NME 2024

*Study preformed under EUROfusion Enabling research project **DeHydroC***

Location of D inside W (defects) - NRA channeling

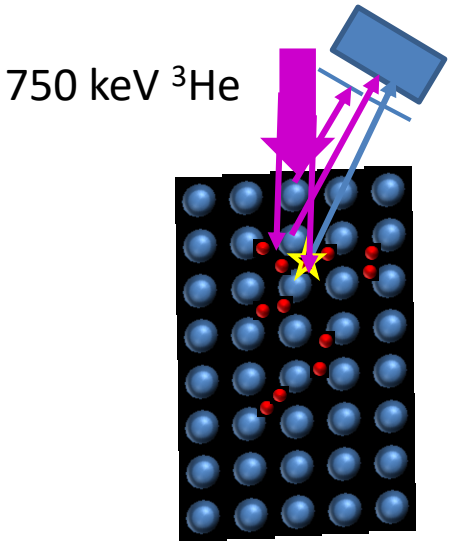
Method to determine hydrogen interstitial sites in metals in 70's/80's
[Fukai, The metal-hydrogen systems, Springer 2005]

- Examples of detection of hydrogen in metals by NRA-channeling by group of Picraux and Myers in Sandia National Laboratories (SNL), New Mexico; Implantation by keV D ions!



Angular scans through the <100> axis on W
- *Deuterium sitting in tetrahedral sites*

Picraux, S. T. & Vook, F. L. Deuterium lattice location in Cr and W. Phys. Rev. Letters 33, 1216 (1974).



Angular scan

But:
- Academic case of defect free(?) tungsten
- Only qualitative measurement
- 30 keV D ions created vacancies by themselves, even possible to determined position of solute atoms, signal should be dominated by trapped D!

Incorporation of NRA-C into RBSADEC code

Incorporation of NRA-C into binary collision approximation code RBSADEC

*[Zhang, S. et al. Physical Review E **94**, (2016)]*

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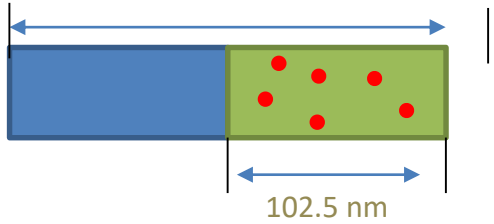
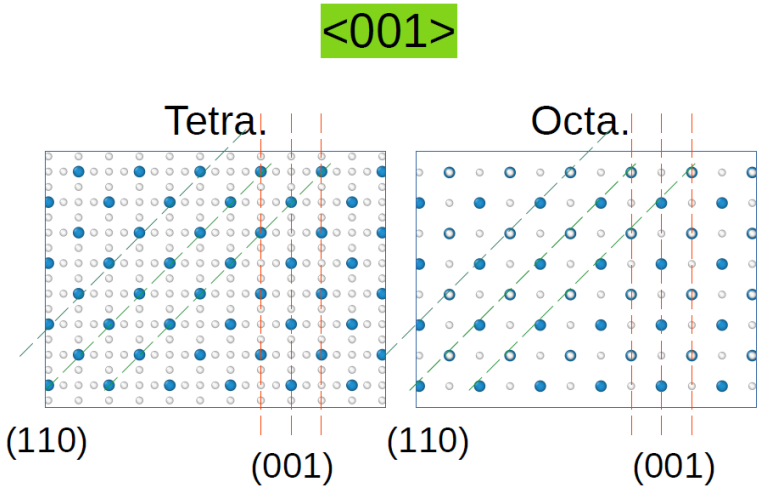
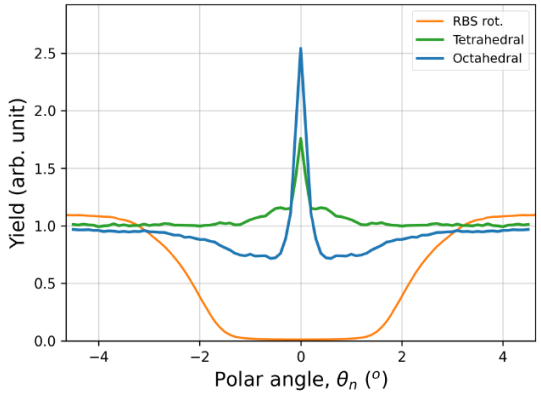
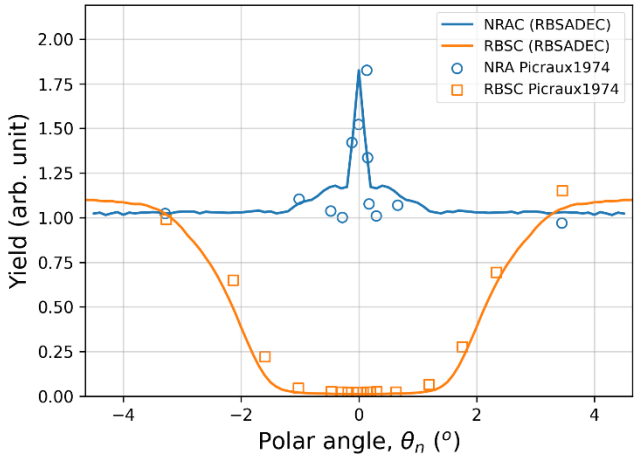
- RBS-C: a pristine W target
- NRA-C:



- 0.1 % of D at tetrahedral sites







S. Picraux, Phys. Rev. Lett., 33, 1974

3×10^{15} cm^{-2} 30 keV D on W

Difference between experiments and simulations: not exactly on tetrahedral sites?

- Hydrogen in vacancies, some position close to tetrahedral sites, etc.

➢ Effect of damage dose: D sites change

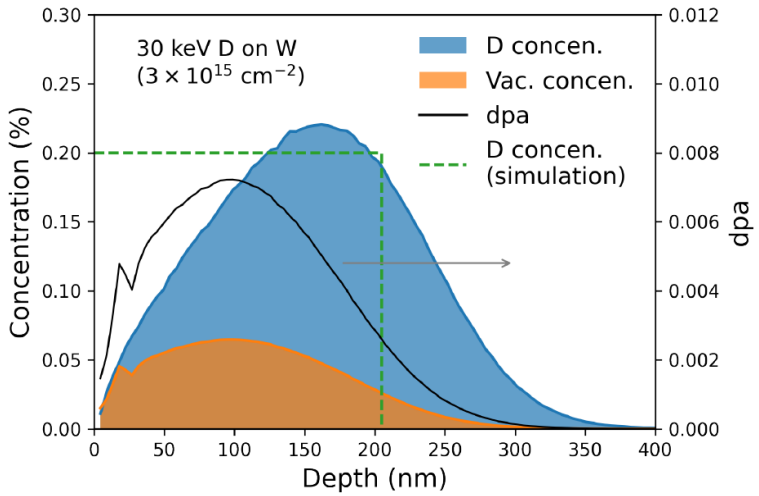
➢ Improving the fit: adjust D locations, D location according to DFT calculations

*Study preformed under EUROfusion Enabling research project **DeHydroC***

Development of C-NRA simulation and detection of D by RBSADEC code

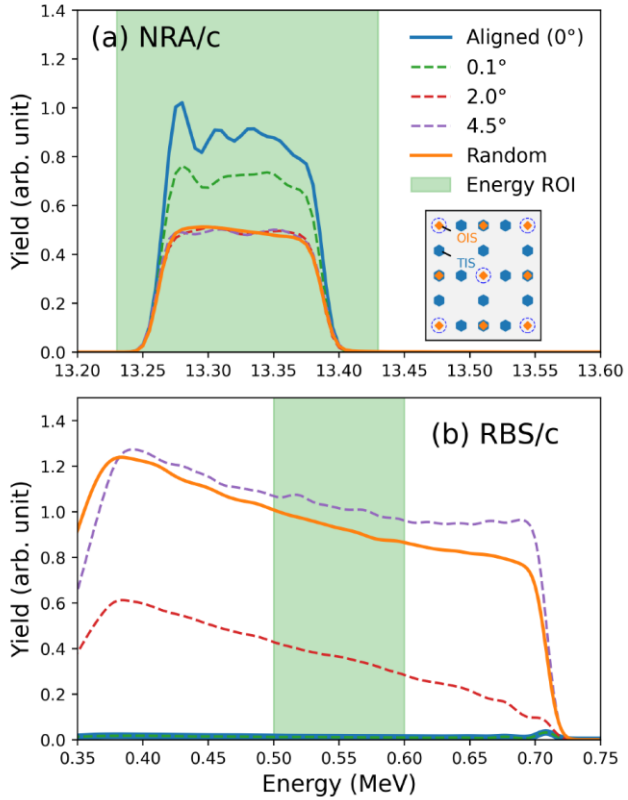
- SRIM calculation of vacancy distribution for 30 keV D ions in W for Picraux experiment

(S. Picraux, Phys. Rev. Lett., 33, 1974)

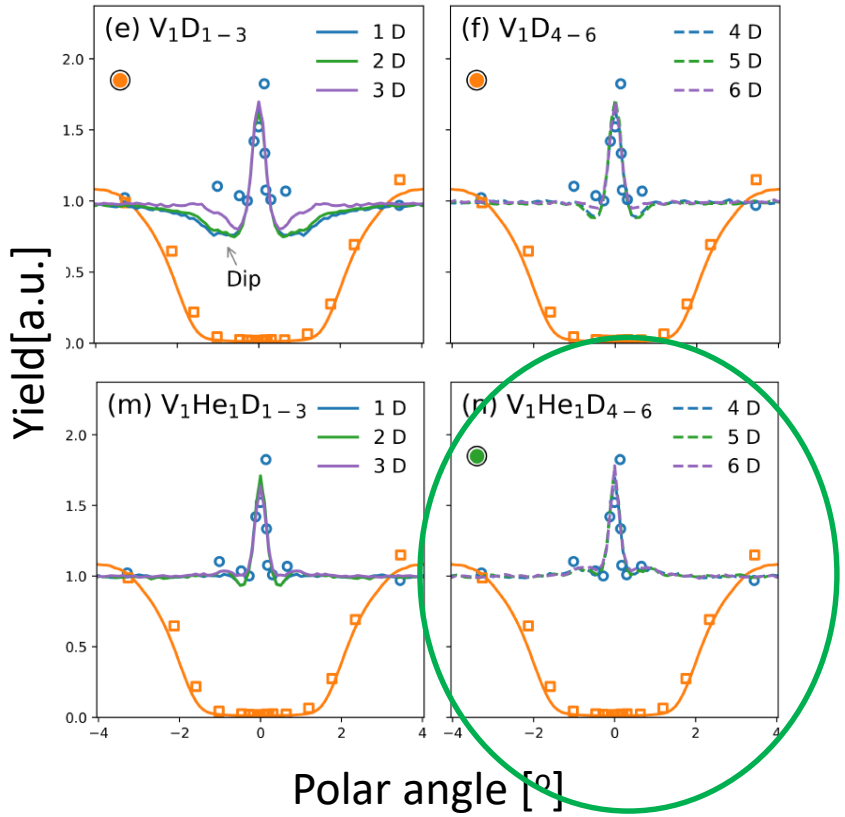


- Creation of vacancies
- Multiple hydrogen occupancy in a vacancy [Heinola et al. PR B (2010), Fernandez et al. Acta Materialia (2015)]

- **Calculation the NRA and RBS yield**



- **Best agreement obtained for He-field vacancy with 5 H atoms**



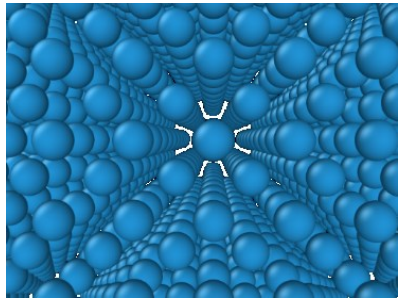
[Jin et al. Phys. Rev. Materials 8, 043604 (2024)]

DeHydroC

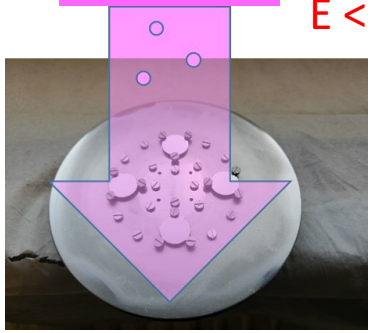
Effort to detect D location in W in defects

Samples: NRA-C tungsten single crystals (100)

Irradiation: 10.8 MeV W ions



W (100)



- **Two damage doses:**

Low ($5.8\times10^{16} m^{-2}$) & High($5.8\times10^{17} m^{-2}$)

SRIM-KP

0.02 dpa **0.2 dpa**

Two temperatures:

290 K & 800 K

Single vacancies and V_2 @ low dose

Vacancy clusters Diff. sizes Vn=25 and 50

'gentle' loading = 'decoration' of defects
ion flux: 6×10^{19} D/(m^2s)
ion fluence: $1\cdot10^{25}$ D/m^2 (48 h)

- W (100) single crystal should show a difference in the C-NRA signal when D is near the octahedral (OIS) or tetrahedral interstitial sites (TIS) [Cabstanjen, H.-D. Phys. Stat. Sol. (a) 59, 11–26 (1980)].

Based on Hu et al. JNM 556 (2022) 153175 – open volume type defects

Sample	Irradiation conditions	Predominant defect expected
78g / #1	0.02 dpa, 290 K	single vacancies
78f / #5	0.2 dpa, 290K	heavily damaged standard
78c / #3	0.02 dpa, 800 K	small vacancy clusters
78b / #2	0.2 dpa, 800 K	big vacancy clusters

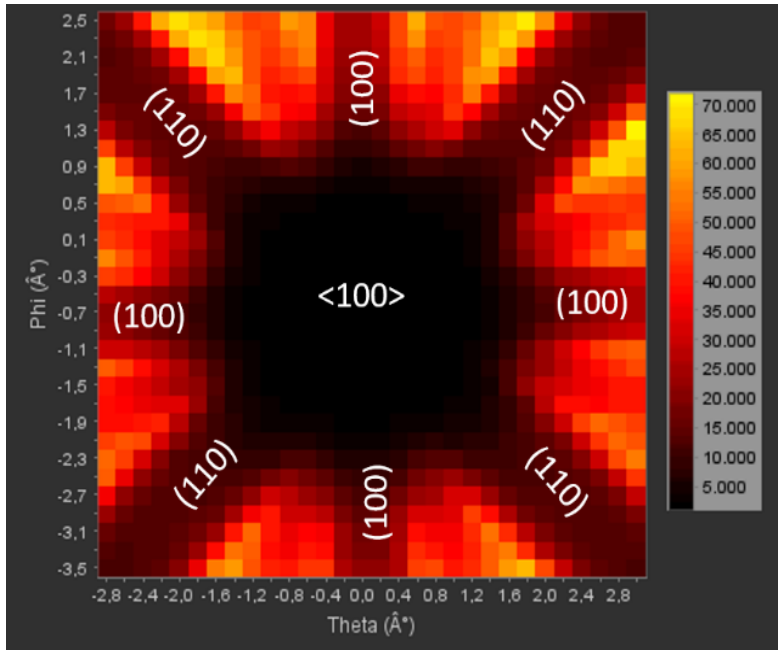
DeHydroC

Markelj et al. NME 39 (2024) 101630
Markelj et al. Acta Materiallia 263 (2024) 119499

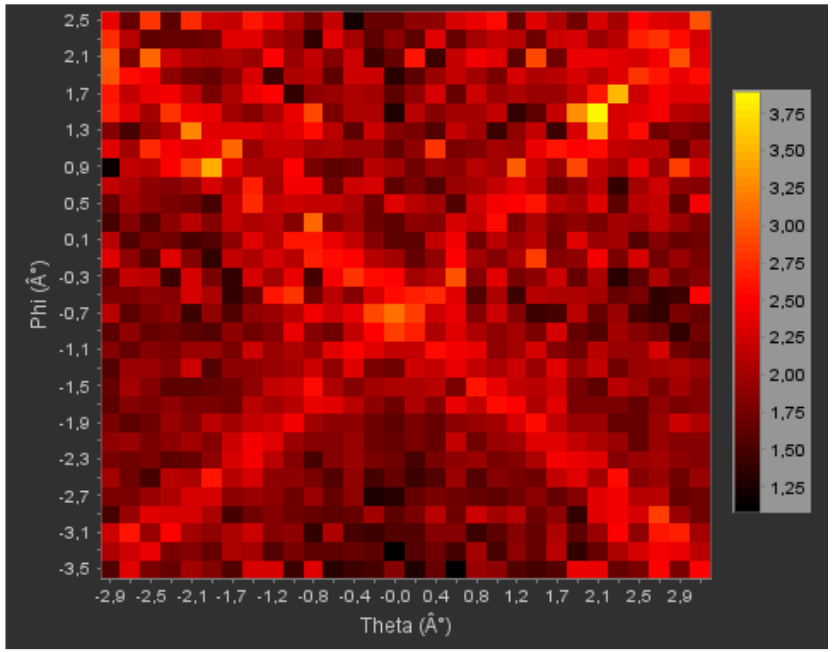
NRA-C and RBS-C: DeHydroC first measurements

^{3}He 0.8 MeV – simultaneous RBS-C and NRA-C 2D maps

2D map for sample #2: 800 K, 0.2 dpa



RBS-C



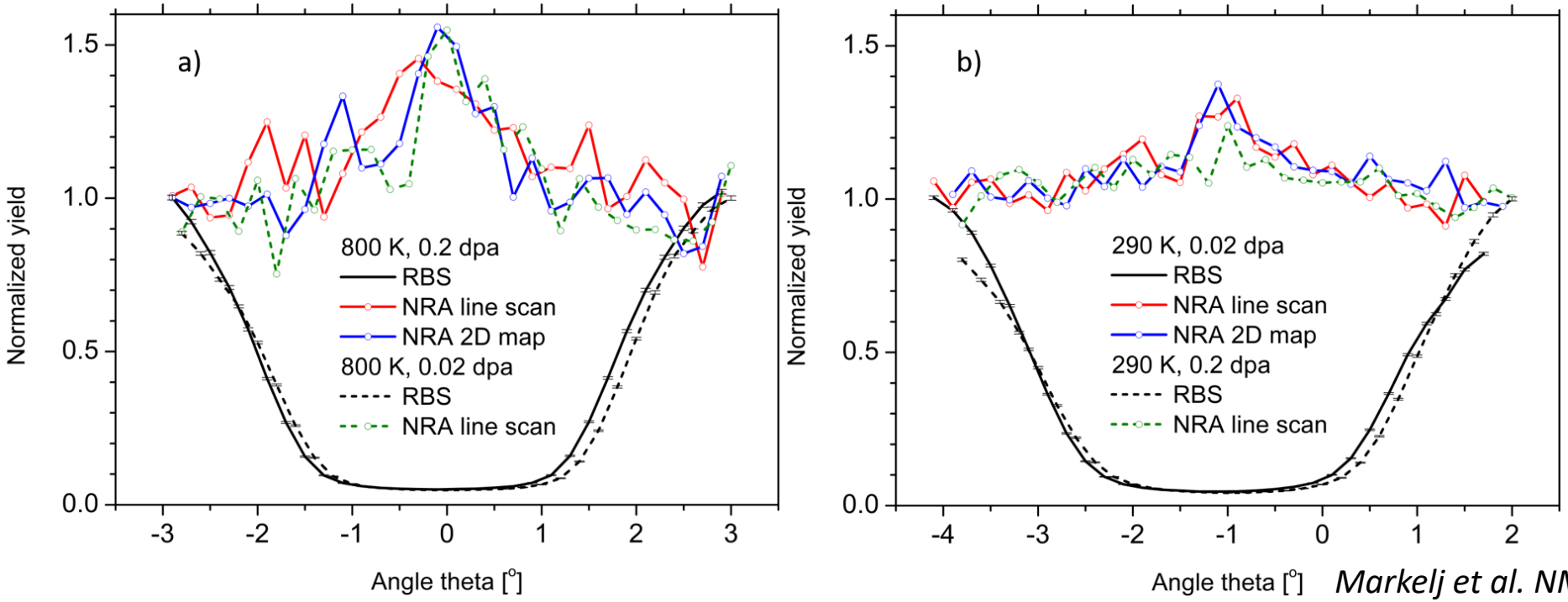
NRA-C

RBS-C was performed at the Hedgehog setup for RBS channeling at Ion Beam Center at HZDR.

Markelj et al. NME 39 (2024) 101630

NRA-C and RBS-C: angular scans

^{3}He 0.8 MeV – simultaneous RBS-C and NRA-C 2D maps



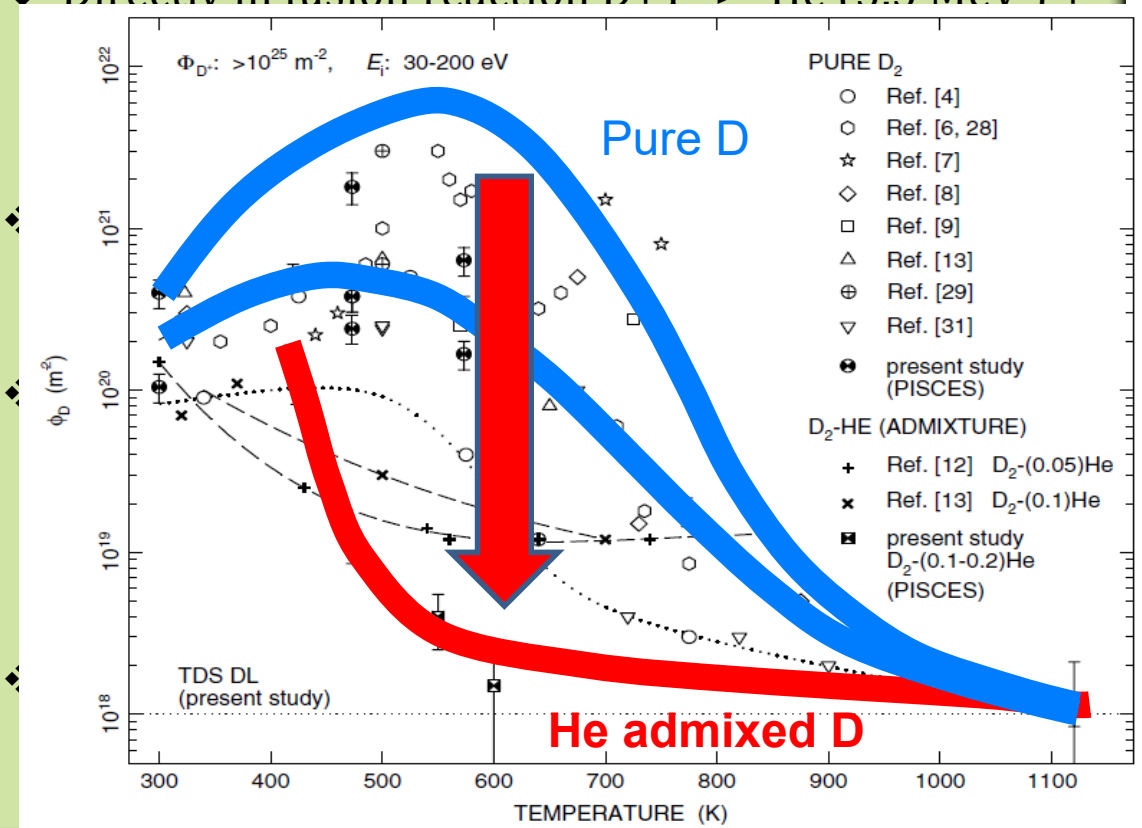
Markelj et al. NME 39 (2024) 101630

- The NRA signal peak for the samples irradiated at 800 K has a <u>wider and higher</u> NRA signal compared to the 0.02 dpa/290 I
- Speculation: vacancy ese clusters has a broader distribution,

Work ongoing:
NRA-C simulations, combination with DFT - multi occupancy of H in vacancy and vacancy clusters

Different sources of He in fusion device

- Directly in fusion reaction D+T -> ^{4}He (3.5 MeV) +

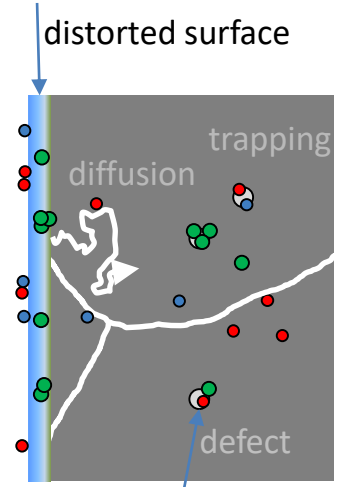


~700 appm

M.J. Baldwin et al. NF 51 (2011) 103021

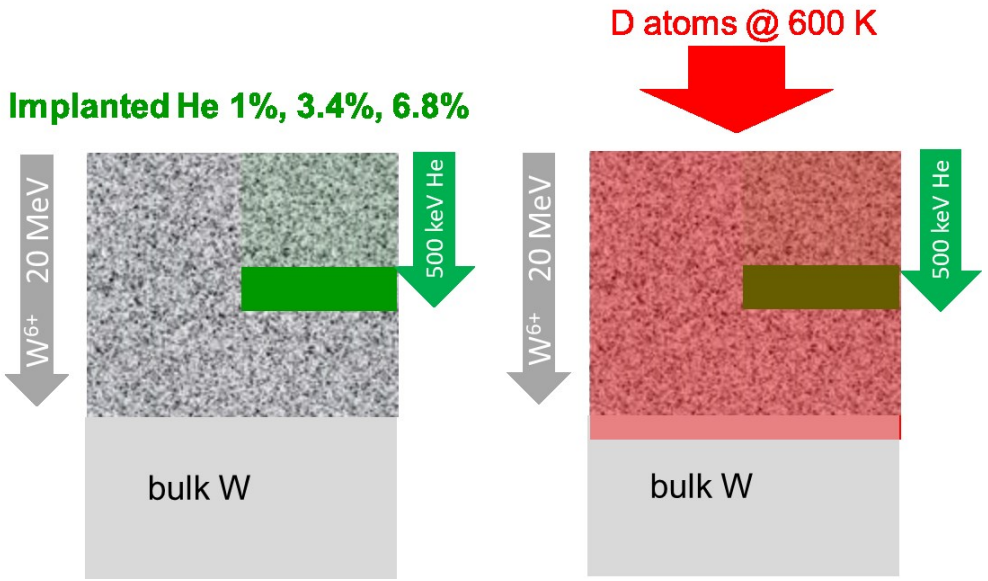
Influence of He on surface ?

Affects the tungsten surface by bubble growth – decrease deuterium/tritium uptake into bulk and retention [Baldwin et al. NF 51 (2011) 103021]



Influence of He in the bulk of tungsten ?

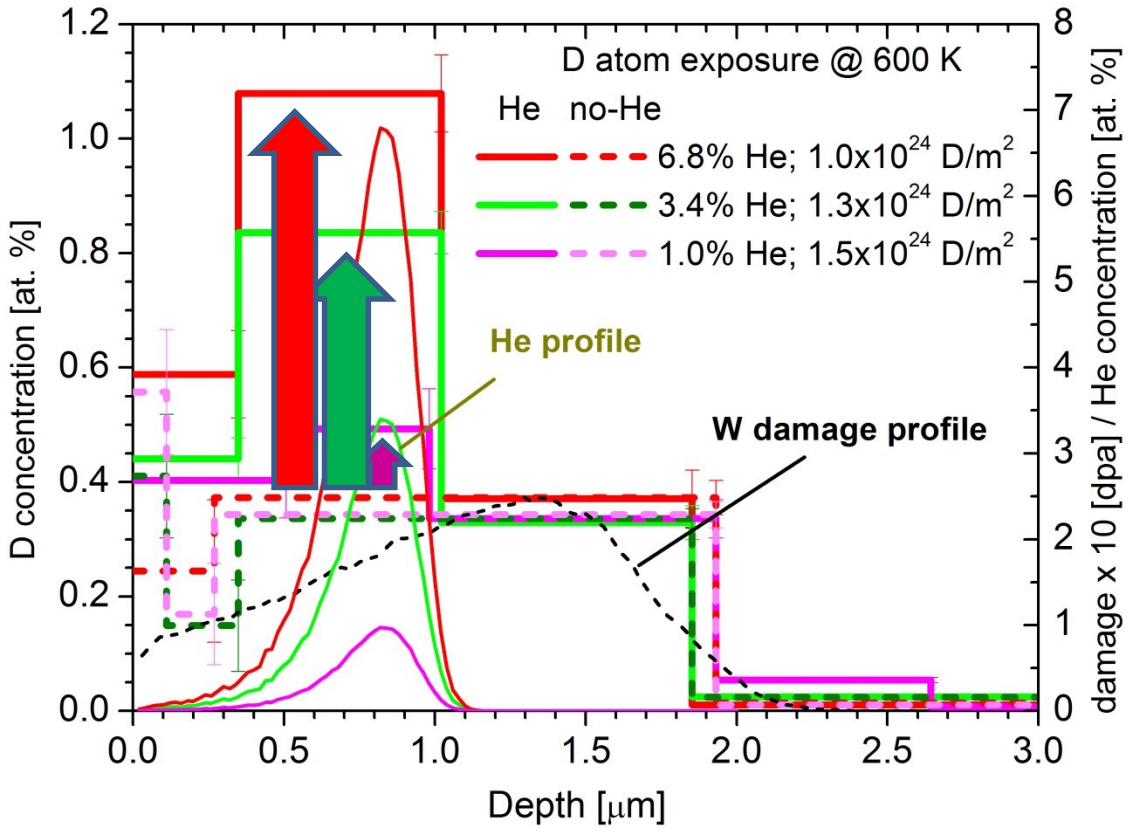
Effect of different He fluences/concentrations on D retention



D depth profiles for different He concentrations

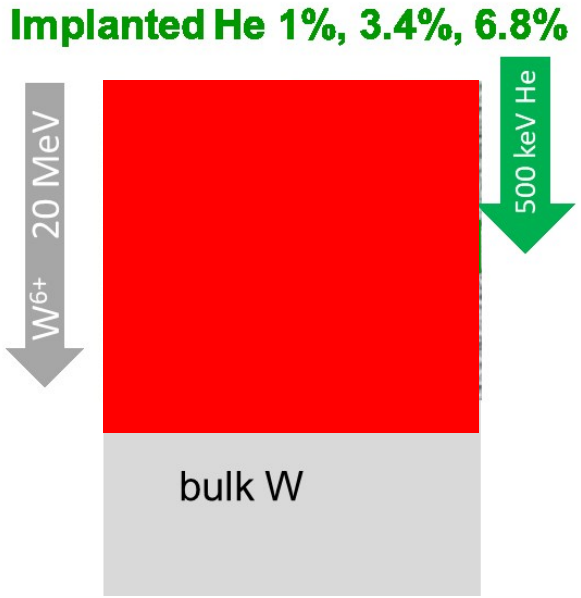
- Observed change of D retention for different He concentrations

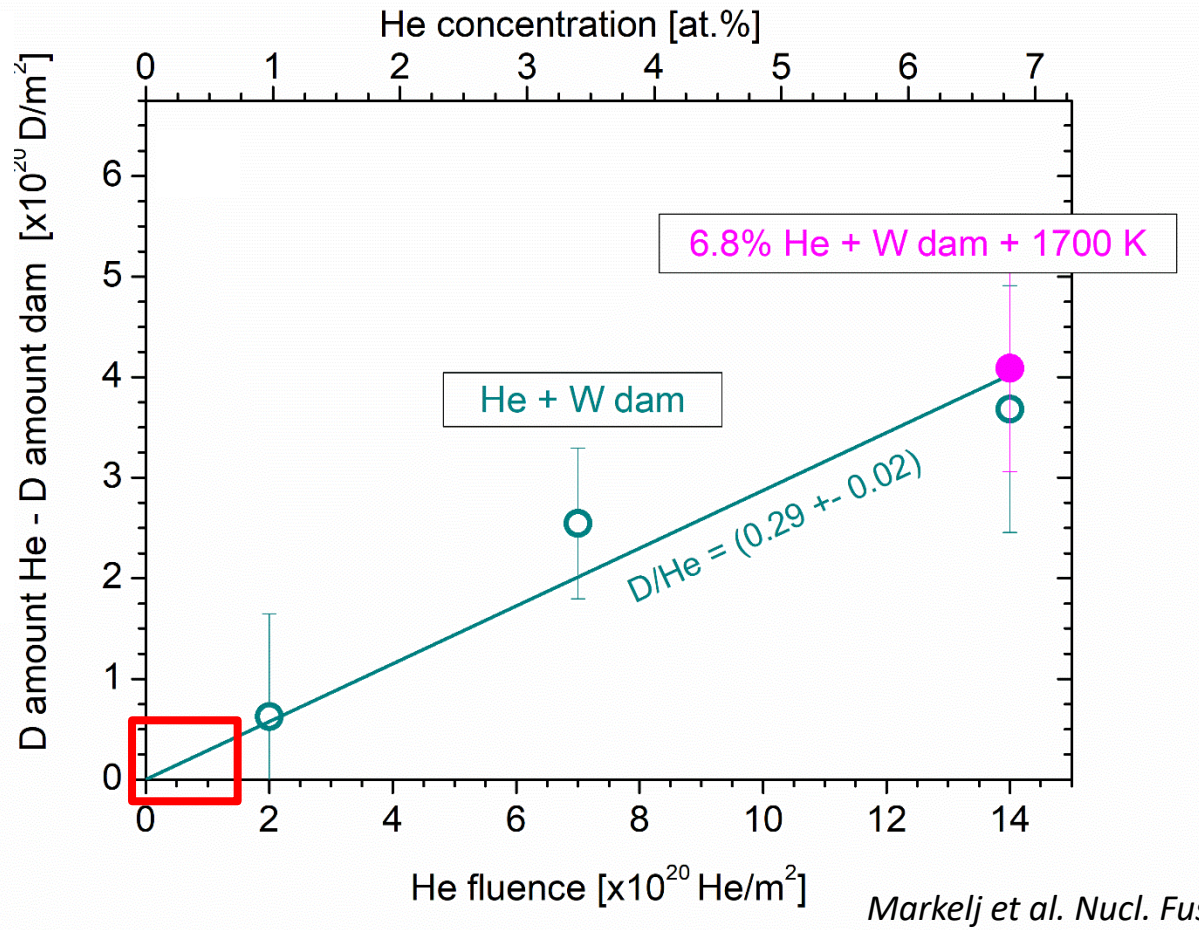
- Increase of D concentration:
  - By 1.4 - 1% He
  - By 2.5 - 3.4% He
  - By 2.9 - 6.8% He
- **No influence of He on D transport in the bulk**



Markelj et al. Nucl. Fusion 60 (2020) 106029

Effect of different bulk He concentrations on D retention

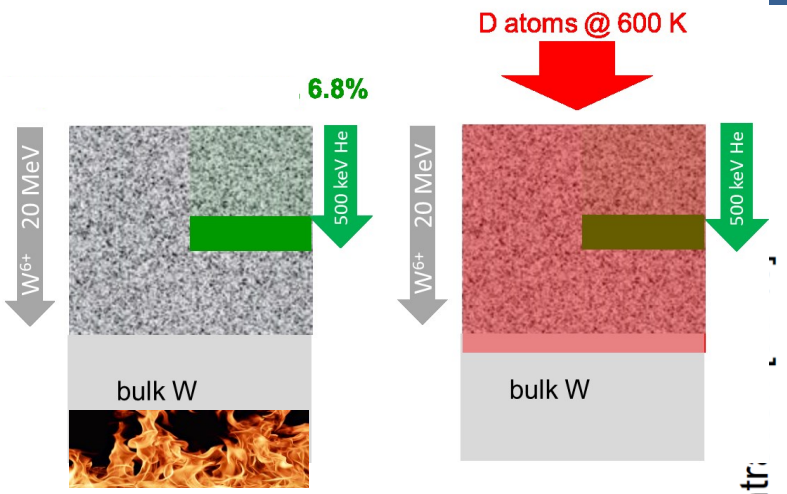


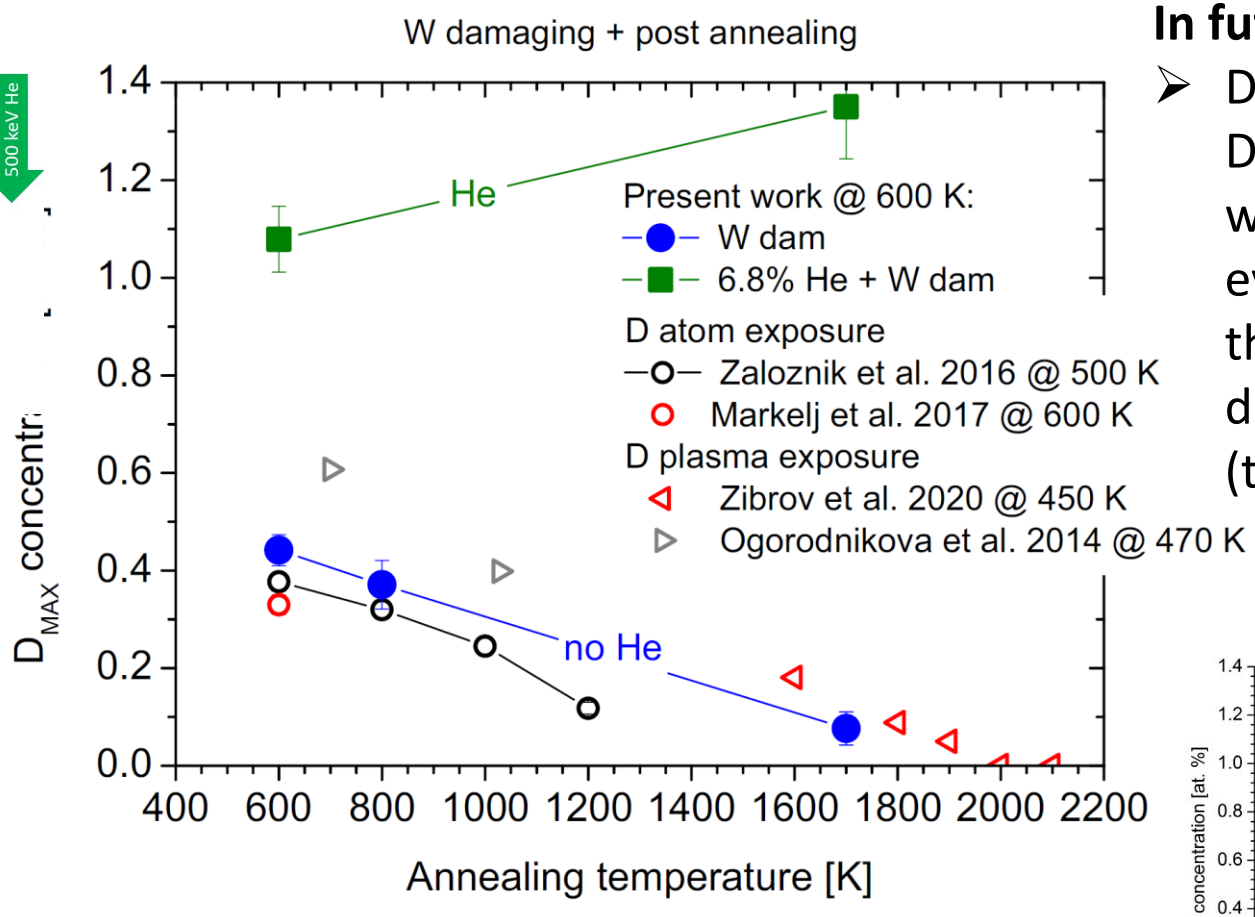


Markelj et al. Nucl. Fusion 60 (2020) 106029

✓ In the main wall of a future fusion device **the effect of He will not dominate D retention** in W since the expected He concentrations in DEMO of ~700 appm are well bellow 1 at. % = 10000 appm

Effect of post-annealing with He on D retention

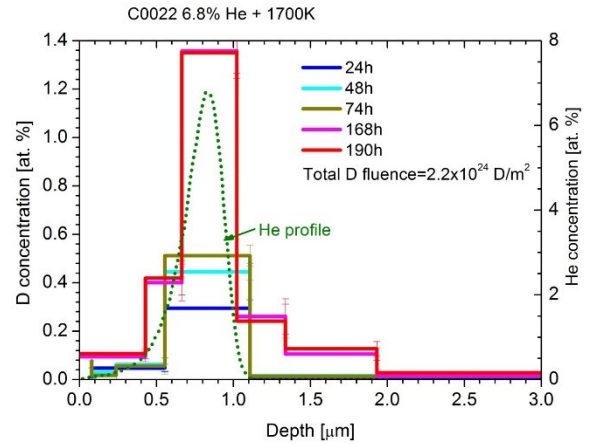




- Annealing to 1700 K – creation of He bubbles ≈ 2 nm size
- **He did not lose the capacity to store D with annealing**
- **He bubbles do not act as transport-barrier**

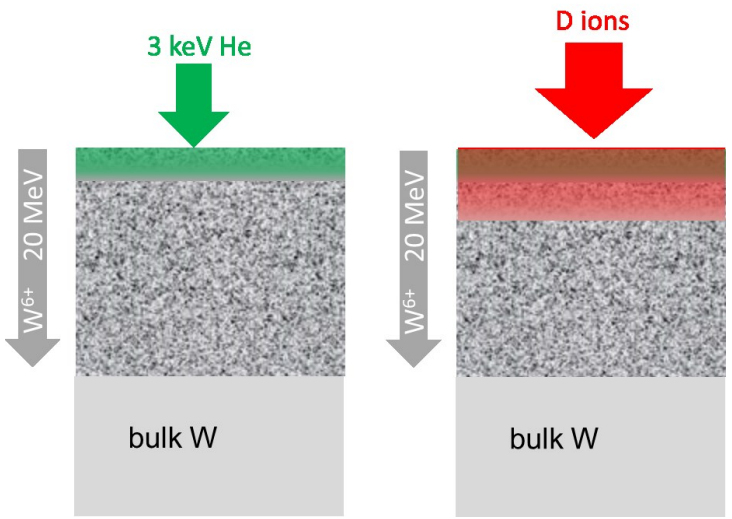
In future fusion device:

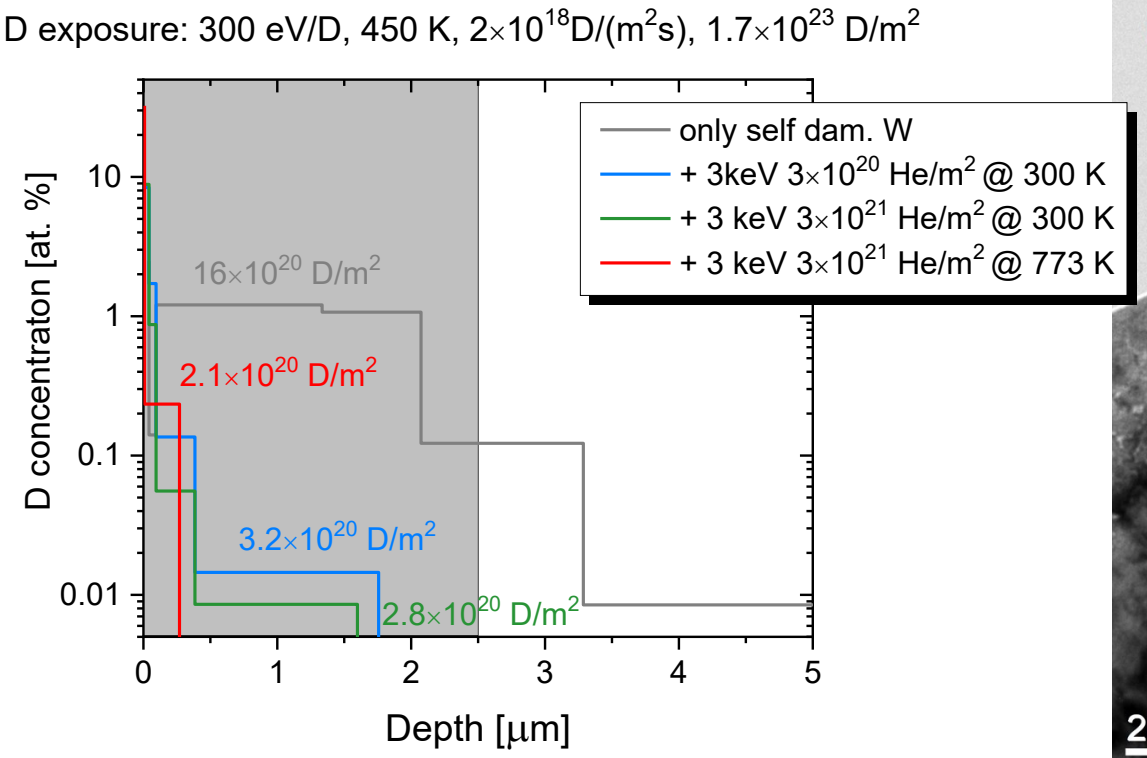
- Due to accumulation of He D retention will increase with time and it could eventually dominate over the effect of displacement damage at high flux (temperature) areas.

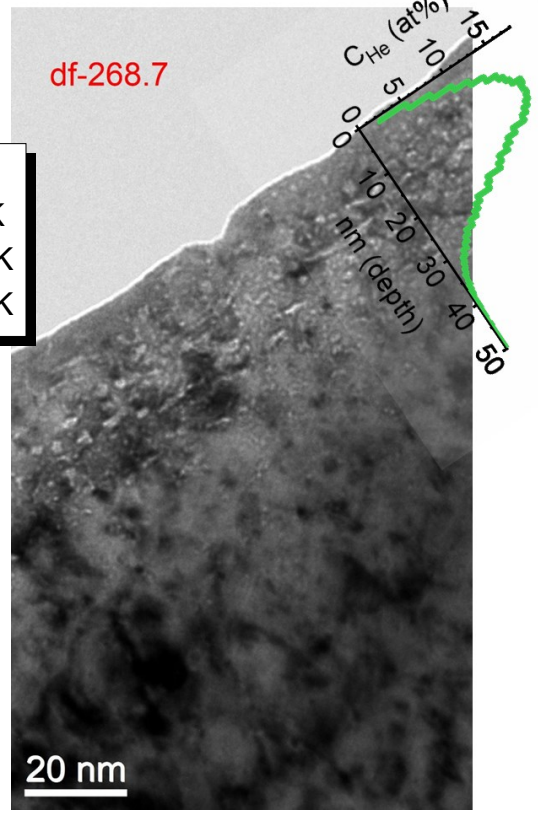


Markelj et al. Nucl. Fusion 60 (2020) 106029

D uptake in He-containing W: NRA



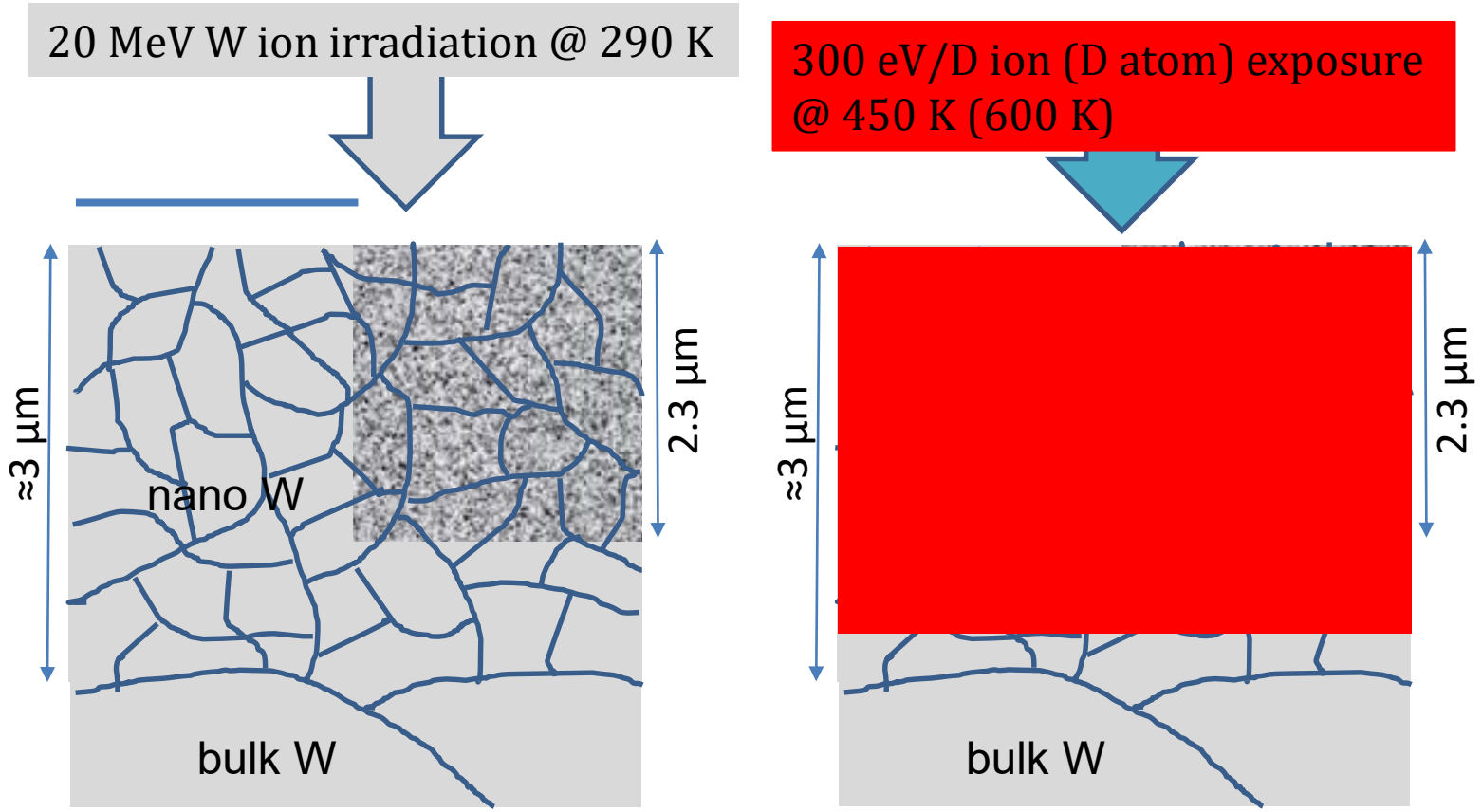




- **Self-damaged W** as 'getter' underneath the He-implantation zone
- For the same fluence D hardly penetrates beyond He implantation zone
- $D_{max} \approx 8$ at.%!
- Nearly unaffected by He fluence
- Nearly unaffected by He exposure temperature
- Decreased deuterium uptake - surface effect - Increased recycling due to 'open porosity'?

Markelj et al. unpublished

The influence of grain boundaries on displacement damage and D retention

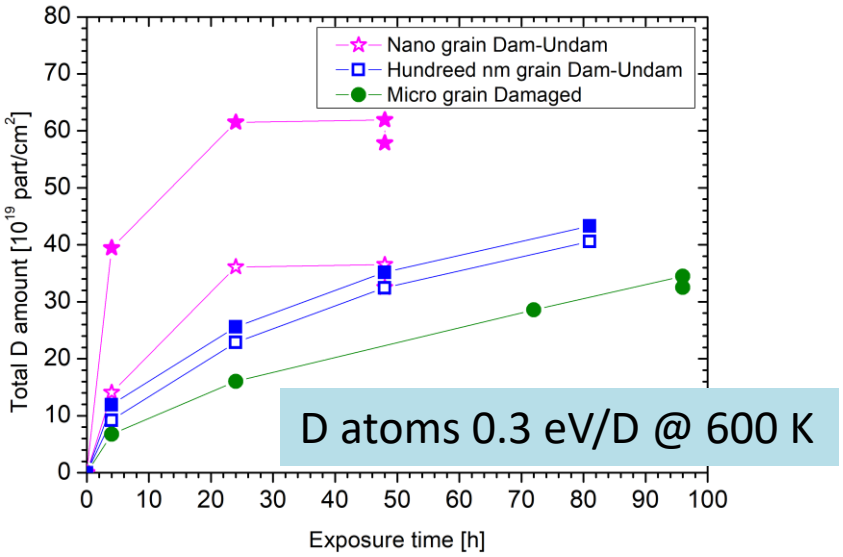


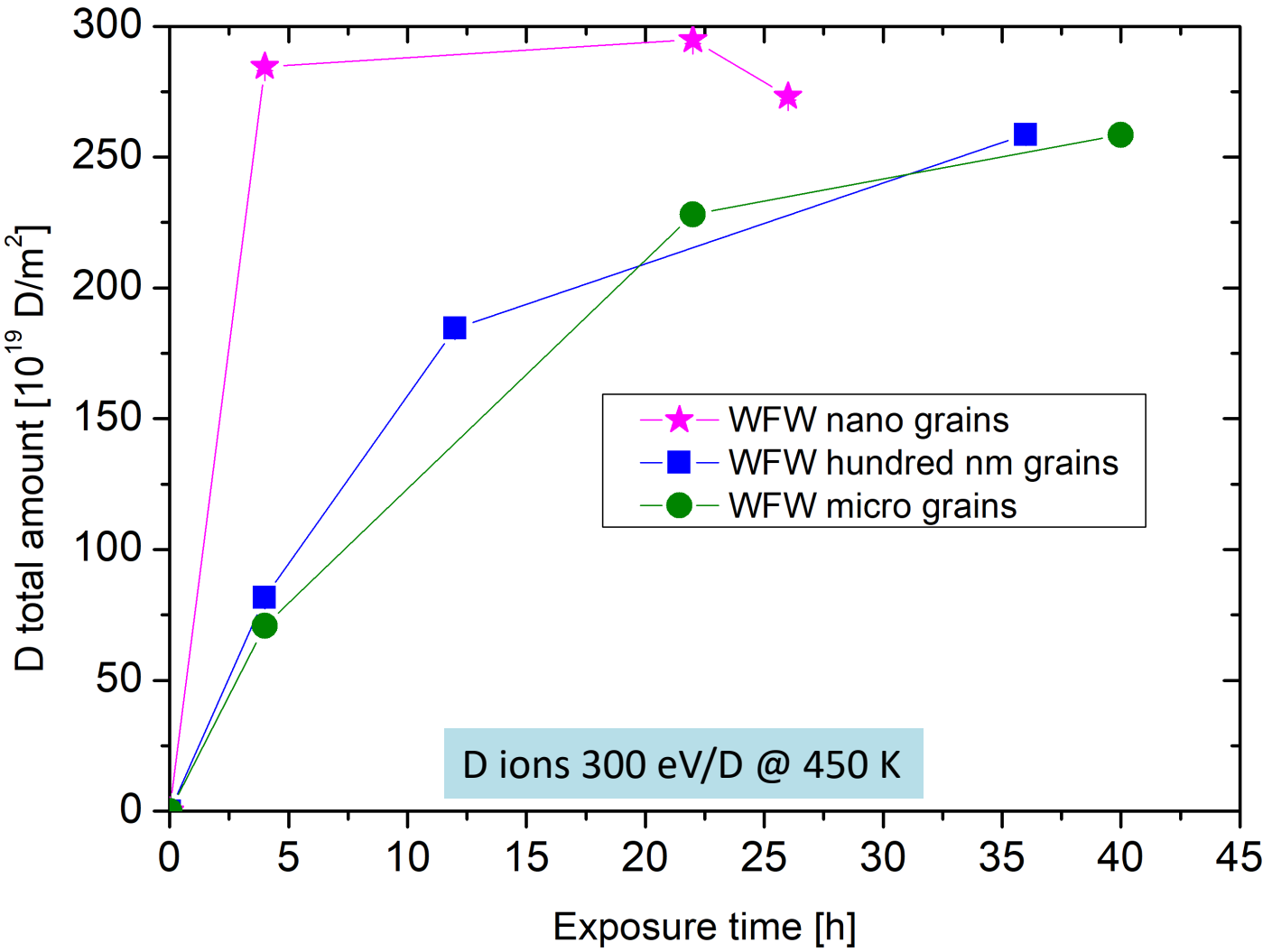
We studied samples with:

- Nanometer grain size (25 nm)
- Hundreed nanometer grain size (80 nm)
- Micrometer grain size (1 µm)

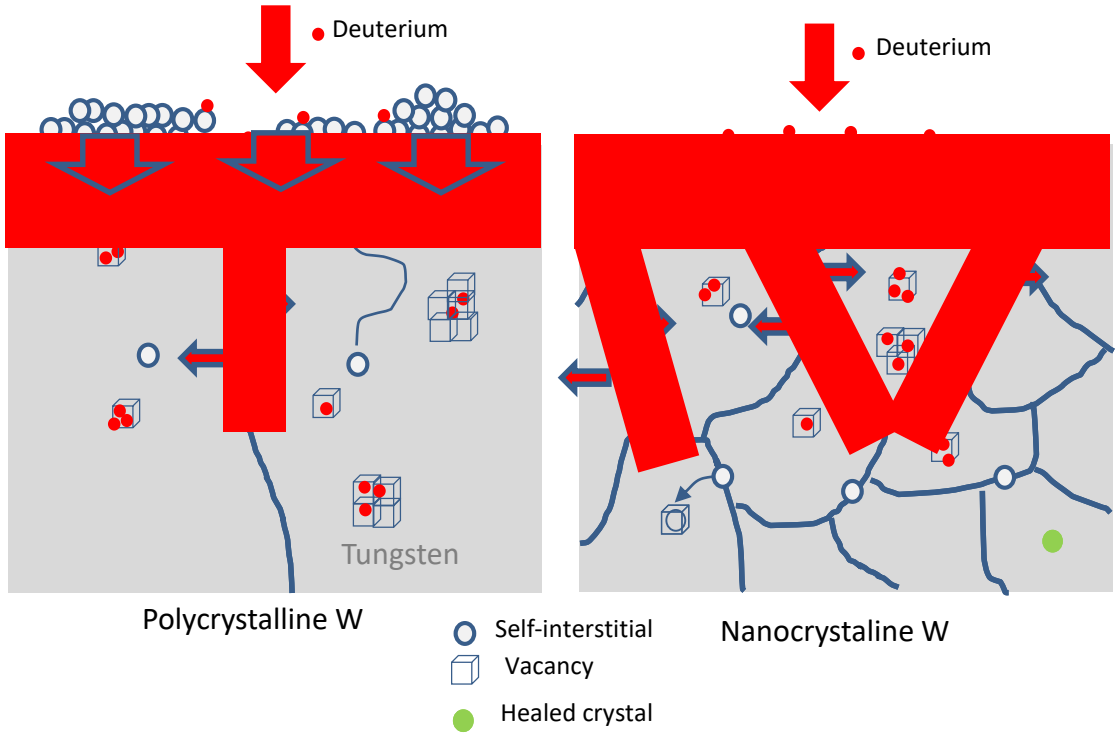
Influence of grain size on D retention and transport

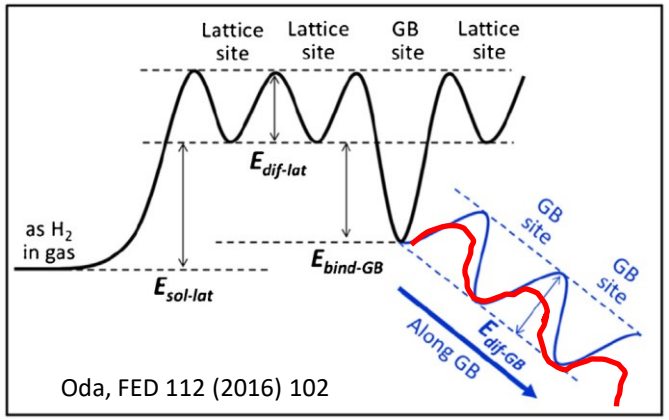
- Saturation of D concentration at ~1.5 at. % in damaged zone
- Similar D concentration for nano and hundred nm grain size
- Size of the grains does influence on the speed of D uptake
- ➢ Diffusion along the grain boundaries [Manhard et al. Hydrogenography]
- The same trend observed for the D atom exposures





Influence of grain size on D transport





Nanocrystalline structure

Influence of grain boundaries (GB) on hydrogen isotope transport

- $E_{dif-lat}$ = 0.28 eV [Holzner et al., Phys. Scr. T171 (2020) 014034]
- GB in polycrystalline W can provide fast and extended transport channel [Toussaint Phys. Scr. T159 (2014) 014058] - depending on the grain.
  - E_{dif-GB} = 0.13 eV [Zhou et al., NF 50 (2010) 025016]
- GB can also be trapping sites for hydrogen isotopes [Oda, FED 112 (2016) 102]
  - $E_{bind-GB}$= 1.1 eV [Zhou et al., NF 50 (2010) 025016]

➢ Even though D diffuses along the grain boundaries, D goes back into the grains and populates the defects within the grains

- GB affect ion and atom transport – Property of the bulk - change of E_{dif} in bulk

Conclusions

- Need for microscopic understanding of the influence of defects on hydrogen isotope retention and vice versa – our approach to separate the defect creation and the effect of D and defects decoration by D
- The effect of D presence on damage creation:
- D presence increases damage creation by more than a factor of 2
- De-trapping energies do not change
- He in the bulk and on the surface:
- He presence at the surface and in the bulk: locally He atoms/clusters/bubbles act as additional traps for deuterium (He/D = 3). D is preferentially retained were the He sits.
- He close to the surface increases locally D retention but leads to a significantly **reduced uptake into depth** by a factor up to 15.
- Grain boundaries
- Influence on the D transport – faster diffusion along the grain boundaries

Conclusions

Open questions:

- Lacking a model on defect annealing – do defects anneal / change during TDS
- Effect of D ion flux on defect creation and evolution at high temperatures
- Hydrogen isotope trapping at different defects – which responsible for fuel retention, do we really know?
- D location around vacancies or vacancy clusters – Very first NRA-C measurements on irradiated W samples with different defect structures show clear difference in the NRA-C response (EUROfusion ***DeHydroC*** project)
  - Modelling is necessary to understand NRA-C experimental results

- Only experiment with modelling hand in hand can bring progress in the field

Acknowledgments

Mitja Kelemen, Janez Zavašnik, Andreja Šestan, Esther Punzon Quijorna, Matic Pečovnik, Anže Založnik, Primož Vavpetič, Primož Pelicon, Iztok Čadež and Zdravko Rupnik

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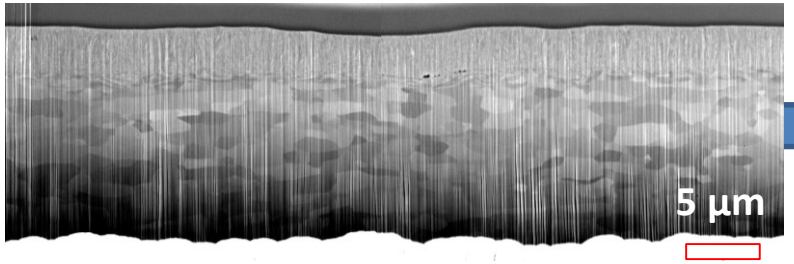
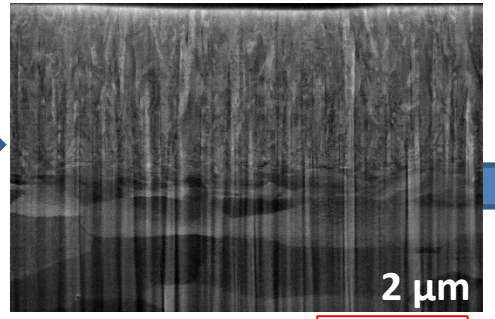
Thank you for your attention

Nanocrystalline samples – grain size

- FIB-SEM images of 3 µm thin W film deposited on W

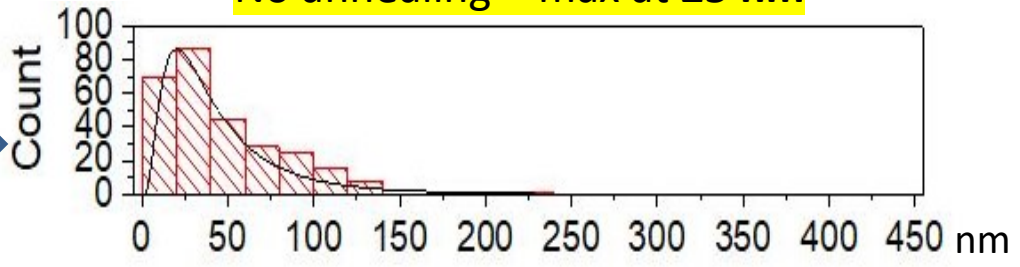
Nanometer grains



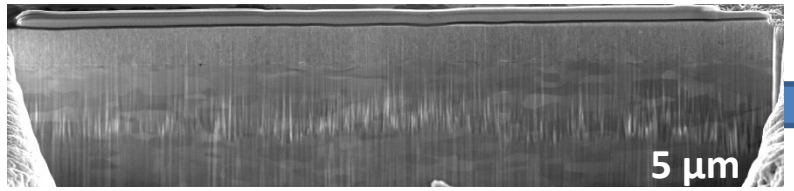


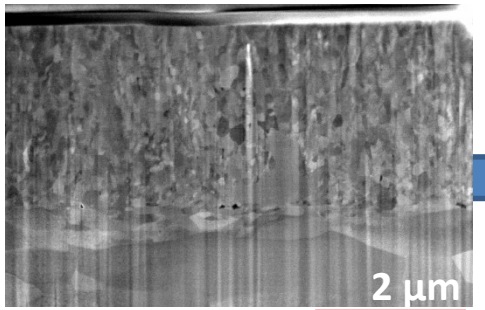
Nanometer grains

No annealing – max at **25 nm**



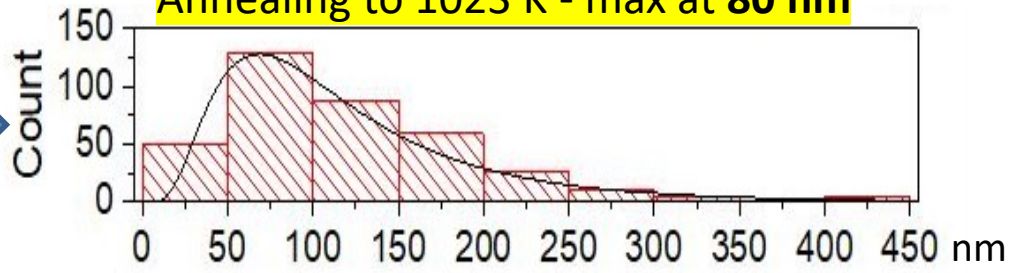
Hundred nanometer grains



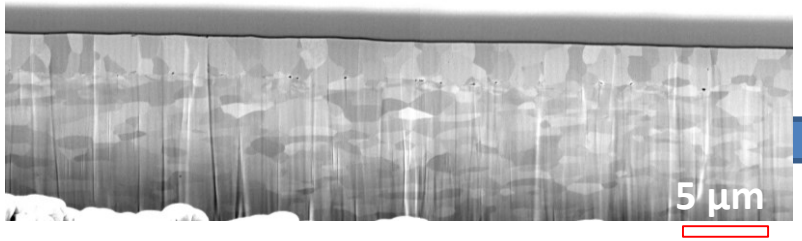


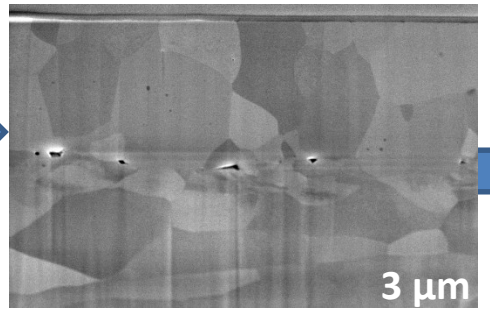
Hundred nanometer grains

Annealing to 1023 K - max at **80 nm**



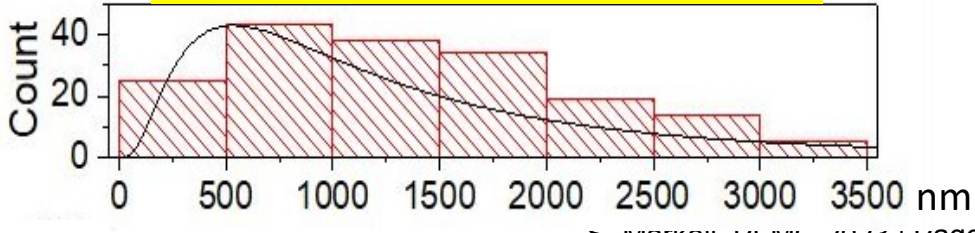
Micrometer grains



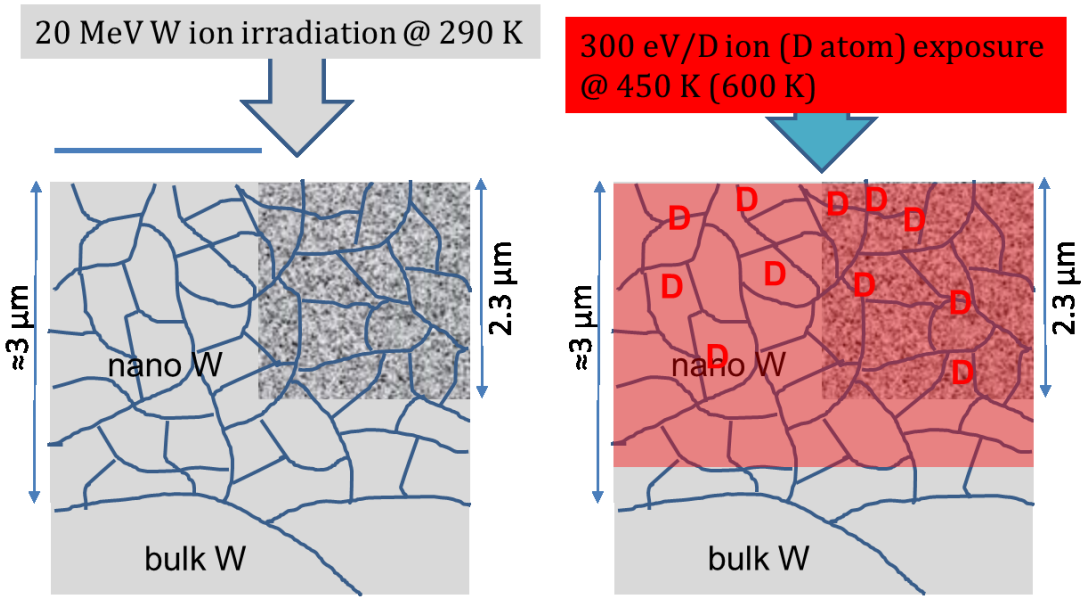


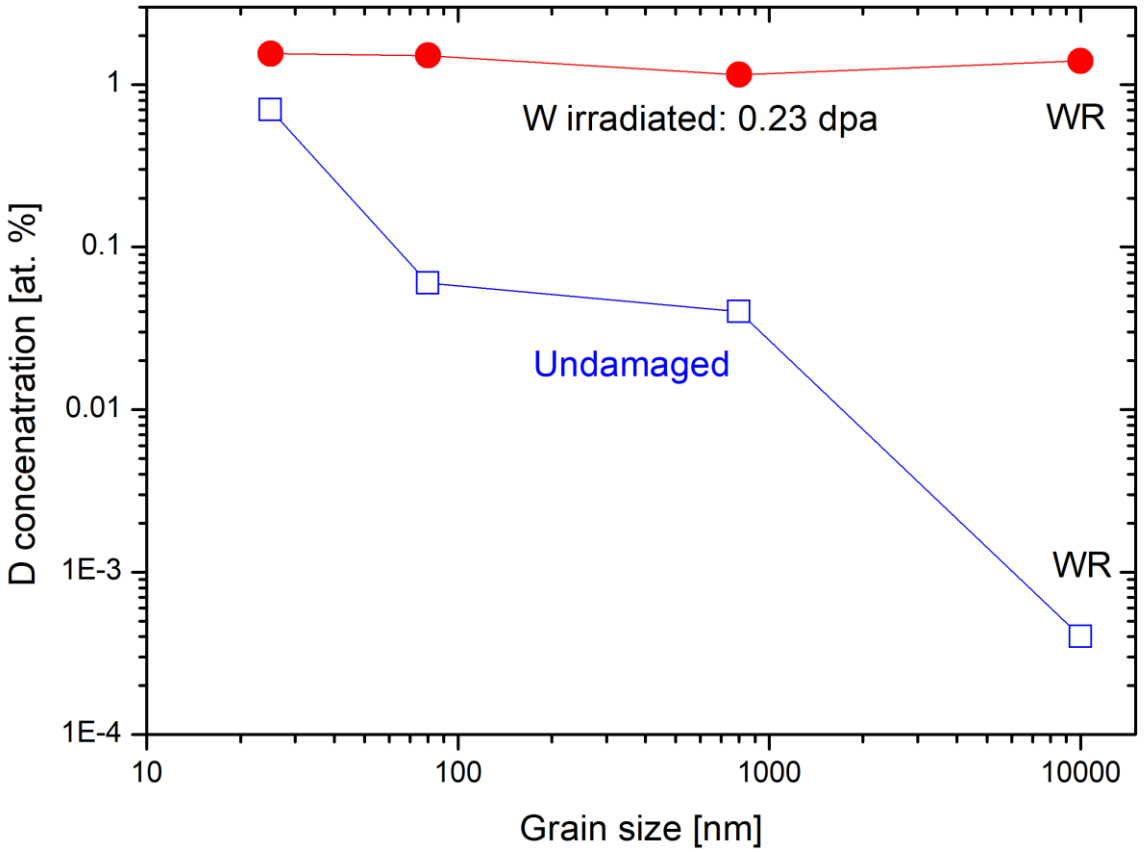
Micrometer grains

Annealing to 1223 K - max at **1 µm**



Influence of grain size on D retention





300 eV D ions exposure at 450 K to exposure time sufficien to fill the damaged layer:

- <u>Saturation of D concentration at ~1.5 at. % in damaged zone</u>
- Similar D concentration for nano and hundred nm grain size
- Lower D concentration for largest grain size sample -similar to recrystallized W

➢ Nanocrystalline material larger D retention - undamaged

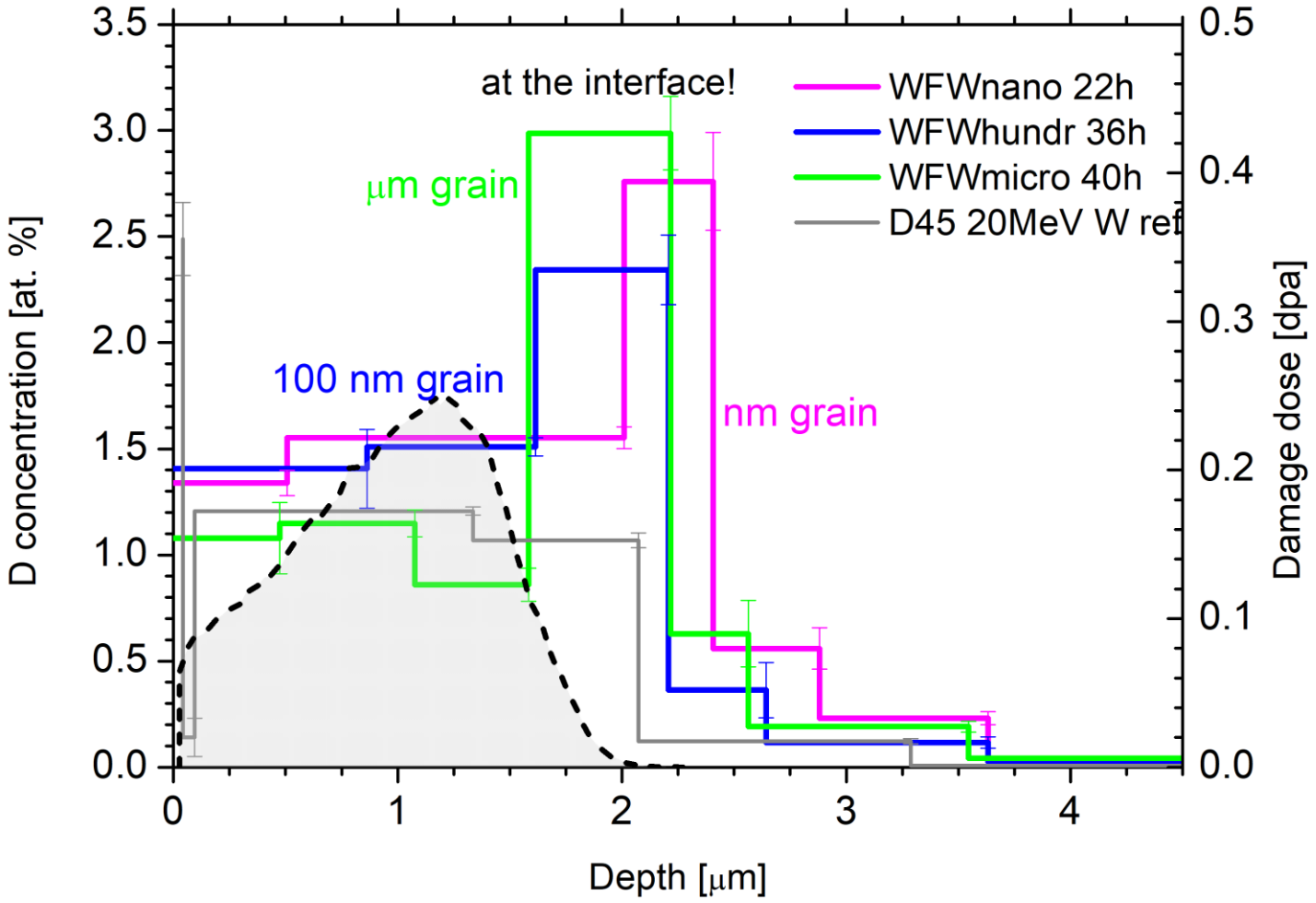
In agreement with [Ogorodnikova, J. Appl. Phys. 122, 044902 (2017)]

D ion exposure – D depth profiles

Influence of grain size on D retention

300 eV D ions exposure at 450 K to exposure time sufficient to fill the damaged layer:

- Saturation of D concentration at ~1.5 at. % in damaged zone
- Similar D concentration for nano and hundred nm grain size
- Lower D concentration for largest grain size sample – but not drastic (similar to W reference)
- Larger D concentration at the interface – oxides, defects?



➢ 1.2-1.4 at. % is the typical D concentration observed for self-damaged W @ 450 K